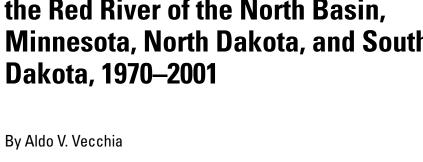


In cooperation with the Bureau of Reclamation

Water-Quality Trend Analysis and Sampling Design for Streams in the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970–2001

Scientific Investigations Report 2005–5224

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Scientific Investigations Report 2005–5224

U.S. Department of the Interior

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Water-Quality Trend Analysis and Sampling Design for Streams in the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970-2001

By Aldo V. Vecchia

Abstract

The Bureau of Reclamation is considering several alternatives to meet the future municipal, rural, and industrial watersupply needs in the Red River of the North (Red River) Basin, and an environmental impact statement is being prepared to evaluate the potential effects of the various alternatives on the water quality and aquatic health in the basin in relation to the historical variability of streamflow and constituent concentration. Therefore, a water-quality trend analysis was needed to determine the amount of natural water-quality variability that can be expected to occur in the basin, to determine if significant water-quality changes have occurred as a result of human activities, to explore potential causal mechanisms for water-quality changes, and to establish a baseline from which to monitor future water-quality trends. This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the Bureau of Reclamation, to analyze historical waterquality trends in two dissolved major ions, dissolved solids, three nutrients, and two dissolved trace metals for nine streamflow-gaging stations in the basin.

Annual variability in streamflow in the Red River Basin was high during the trend-analysis period (1970-2001). The annual variability affects constituent concentrations in individual tributaries to the Red River and, in turn, affects constituent concentrations in the main stem of the Red River because of the relative streamflow contribution from the tributaries to the main stem. Therefore, an annual concentration anomaly, which is an estimate of the interannual variability in concentration that can be attributed to long-term variability in streamflow, was used to analyze annual streamflow-related variability in constituent concentrations. The concentration trend is an estimate of the long-term systematic changes in concentration that are unrelated to seasonal or long-term variability in streamflow. Concentrations that have both the seasonal and annual variability removed are called standardized concentrations. Numerous changes that could not be attributed to natural streamflowrelated variability occurred in the standardized concentrations during the trend-analysis period. During various times from the late 1970's to the mid-1990's, significant increases occurred in standardized dissolved sulfate, dissolved chloride, and dissolved-solids concentrations for eight of the nine stations for which water-quality trends were analyzed. Significant increases also occurred from the early 1980's to the mid-1990's for standardized dissolved nitrite plus nitrate concentrations for the main-stem stations. The increasing concentrations for the mainstem stations indicate the upward trends may have been caused by human activities along the main stem of the Red River. Significant trends for standardized total ammonia plus organic nitrogen concentrations occurred for most stations. The fitted trends for standardized total phosphorus concentrations for one tributary station increased from the late 1970's to the early 1980's and decreased from the early 1980's to the mid-1990's. Small but insignificant increases occurred for two main-stem stations. No trends were detected for standardized dissolved iron or dissolved manganese concentrations. However, the combination of extreme high-frequency variability, few data, and the number of censored values may have disguised the streamflow-related variability for iron.

The time-series model used to detect historical concentration trends also was used to evaluate sampling designs to monitor future water-quality trends. Various sampling designs were evaluated with regard to their sensitivity to detect both annual and seasonal trends during three 4-month seasons. A reasonable overall design for detecting trends for all stations and constituents consisted of eight samples per year, with monthly sampling from April to August and bimonthly sampling from October to February.

Introduction

The Red River of the North (hereinafter referred to as the Red River) begins at the confluence of the Bois de Sioux and Otter Tail Rivers south of Wahpeton, N. Dak. (fig. 1), and flows northward to Hudson Bay, draining parts of Minnesota, North Dakota, South Dakota, Manitoba, and Saskatchewan. The Red River Basin at Emerson, Manitoba, encompasses about

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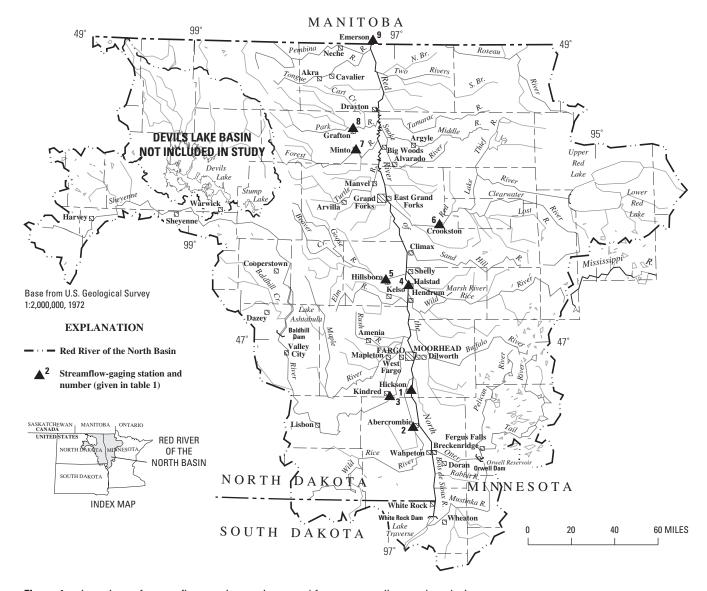


Figure 1. Locations of streamflow-gaging stations used for water-quality trend analysis.

35,000 square miles of rich agricultural lands, forests, wetlands, and prairies and contains numerous lakes and prairie potholes. The physiography, geology, soils, and climate of the basin in Minnesota, North Dakota, and South Dakota are described by Stoner and others (1993).

The Bureau of Reclamation is considering several alternatives to meet the future municipal, rural, and industrial water-supply needs in the Red River Basin, and, in compliance with the National Environmental Policy Act (NEPA), an environmental impact statement is being prepared to evaluate the potential effects of the various alternatives on the water quality and aquatic health in the basin in relation to the historical variability in streamflow and constituent concentration. Therefore, a water-quality trend analysis was needed (1) to determine the amount of natural water-quality variability that can be expected

to occur in the basin, (2) to determine if significant water-quality changes have occurred as a result of human activities, (3) to explore potential causal mechanisms for water-quality changes, and (4) to establish a baseline from which to monitor future water-quality trends. The alternatives being considered include no action, various methods to use water resources that presently (2005) exist in the basin, and various methods to import water from the Missouri River Basin (U.S. Department of the Interior, Bureau of Reclamation, 2005). If an economically feasible and environmentally acceptable alternative is identified, a waterquality monitoring program will be needed to provide the data necessary to maintain compliance with water-quality standards. However, even if the no-action alternative is selected, a waterquality monitoring program will be needed to monitor future water-quality trends in the basin for human-health, ecological, aesthetic, and recreational concerns. To monitor the future

water-quality trends at the lowest cost, an efficient sampling design was needed for streams in the basin. However, the need to monitor the future water-quality trends must be balanced against the cost of obtaining the necessary data. The costs of water-quality sampling and laboratory analysis have increased in recent years, but the budgets for long-term water-quality monitoring have not necessarily increased.

Purpose and Scope

This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the Bureau of Reclamation, to analyze historical water-quality trends in selected constituents and selected streams in the Red River Basin and to develop an efficient sampling design to monitor future trends. The focus of this report is on the Red River upstream from Emerson, Manitoba. The water-quality trends were interpreted in relation to natural (hydroclimatically induced) variability in streamflow and constituent concentration. Natural variability in constituent concentration as a result of variability in streamflow was identified and separated from variability that presumably resulted from human activities. Human activities that may cause water-quality trends include land-use changes, agricultural practices, livestock production, and urban or industrial development. Although a complete interpretation of detected waterquality trends in relation to human activities was beyond the scope of this report, some potential causes for the trends are indicated for possible further investigation.

The constituents evaluated for this report include two dissolved major ions (sulfate and chloride), dissolved solids, three nutrients (dissolved nitrite plus nitrate as nitrogen, total ammonia plus organic nitrogen, and total phosphorus), and two dissolved trace metals (iron and manganese). The constituents were evaluated for nine stations in the Red River Basin, including three stations on the main stem of the Red River and six stations on tributaries to the Red River. All of the constituents were evaluated for four of the stations. However, for the remaining stations, few data are available for some of the constituents. Therefore, for those stations, constituents were evaluated on the basis of data availability.

The water-quality trend analysis and sampling-design results described in the report are based on streamflow and concentration data for 1970-2001. The data were obtained from the U.S. Geological Survey's National Water Information System (NWIS) and were collected through many Federal, State, and local programs, including the U.S. Geological Survey National Stream Water Quality Accounting Network (NASQAN) program, the Hydrologic Benchmark Network program, the National Water Quality Assessment (NAWQA) program, and ongoing cooperative water programs with the North Dakota Department of Health, the Minnesota Pollution Control Agency, and other State and local agencies. Sample-collection techniques and laboratory analyses followed strict, well-documented U.S. Geological Survey protocols (Wilde and others, 1998). A description of the available streamflow and concentration data for the study area is given by Macek-Rowland and Dressler (2002).

Streamflow Data and Hydrologic Characteristics

The locations of the nine U.S. Geological Survey streamflow-gaging stations used for the water-quality trend analysis are shown in figure 1. The stations were selected on the basis of the availability of long-term streamflow and concentration data. Selected station characteristics are given in table 1. Contributing drainage areas for the stations range from about 620 square miles for the Forest River at Minto, N. Dak., station (site 7) to about 35,000 square miles for the Red River at Emerson, Manitoba, station (site 9). Streamflow at most of the stations is affected to various degrees by reservoir regulation, but no major changes in regulation occurred during the trend-analysis period.

Mean annual precipitation for the Red River Basin ranges from about 17 inches in the extreme western part of the basin to about 26 inches in the extreme eastern part of the basin. Precipitation across the basin generally increases from southwest to northeast (Stoner and others, 1993). Actual evapotranspiration from the basin also generally increases from southwest to northeast but at a lesser rate than precipitation. Thus, mean annual runoff (streamflow per unit of drainage area) from the basin also increases in that direction. For the stations given in table 1, mean annual runoff ranged from about 1.2 inches for the Wild Rice River near Abercrombie, N. Dak., station (site 2) to about 3.9 inches for the Red Lake River at Crookston, Minn., station (site 6).

Seasonal variability in streamflow in the Red River Basin is high. Generally, high flows occur during spring and early summer (primarily from snowmelt or rainfall runoff from spring storms) and low flows occur during late fall and winter (primarily from ground-water or reservoir discharges). Seasonal variability was higher for the North Dakota tributaries than for the Minnesota tributaries because of the many lakes and wetlands in Minnesota. For the Abercrombie station (site 2), daily streamflows for April were about 162 times larger, on average, than daily streamflows for January. Daily streamflows for April were 490 cubic feet per second, and daily streamflows for January were 3 cubic feet per second. For the Crookston station (site 6), daily streamflows for April were about six times larger, on average, than daily streamflows for January. Daily streamflows for April were 3,130 cubic feet per second, and daily streamflows for January were 540 cubic feet per second.

Annual variability in streamflow in the Red River Basin also is high. The annual variability, which was particularly high during the trend-analysis period, affects constituent concentrations in individual tributaries to the Red River and, in turn, affects constituent concentrations in the main stem of the Red

4 Water-Quality Trend Analysis and Sampling Design for Streams in the Red River of the North Basin

Table 1. Selected characteristics of streamflow-gaging stations used for water-quality trend analysis.

Site number figure 1)	U.S. Geological Survey station Station name number		Approximate contributing drainage area (square miles)	Mean daily streamflow for 1970-2001 (cubic feet per second)	Latitude	Longitude
1	05051522	Red River of the North at Hickson, North Dakota	4,300	730	46°39'35"	96°47'44'
2	05053000	Wild Rice River near Abercrombie, North Dakota	1,490	127	46°28'05"	96°47'00'
3	05059000	Sheyenne River near Kindred, North Dakota	3,020	298	46°37'54"	97°00'01'
4	05064500	Red River of the North at Halstad, Minnesota	18,000	2,210	47°21'07"	96°50'36
5	05066500	Goose River at Hillsboro, North Dakota	1,090	130	47°24'34"	97°03'39'
6	05079000	Red Lake River at Crookston, Minnesota	5,270	1,490	47°46'32"	96°36'33
7	05085000	Forest River at Minto, North Dakota	620	56	48°16'10"	97°22′10
8	05090000	Park River at Grafton, North Dakota	690	69	48°25'29"	97°24'42
9	05102500	Red River of the North at Emerson, Manitoba	35,000	5,360	49°00'30"	97°12'40

River because of the relative streamflow contribution from the tributaries to the main stem. Mean daily streamflows for the nine stations used for the water-quality trend analysis are given in table 2 along with mean daily streamflows for four additional stations. Because few concentration data are available for the four additional stations, water-quality trends could not be determined for those stations. Therefore, the additional stations were not included in the water-quality trend analysis. However, the tributaries on which the stations are located (the Bois de Sioux River in Minnesota, North Dakota, and South Dakota, and the Otter Tail, Buffalo, and Wild Rice Rivers in Minnesota; fig. 1) provide a substantial part of the streamflow for the main stem of the Red River and, thus, were expected to significantly affect water quality at the main-stem stations. The periods given in table 2 were selected to illustrate the extreme annual variability in streamflow that occurred, both spatially and temporally, during the trend-analysis period. The driest year for most stations was 1977, and the wettest year for most stations was 1997.

Streamflows for the North Dakota tributary stations totaled about 2,840 cubic feet per second during 1997 and about 95 cubic feet per second during 1977 for a ratio of about 30 to 1. Streamflows for the Minnesota tributary stations totaled about 5,000 cubic feet per second during 1997 and about 600 cubic feet per second during 1977 for a ratio of about 8 to 1. Although both ratios were large, the ratio was much larger for the North Dakota tributary stations than for the Minnesota tributary stations. Combined streamflow for the North Dakota tributary stations was about 57 percent of combined streamflow for the Minnesota tributary stations during 1997 and about 16 percent of combined streamflow for the Minnesota tributary stations during 1977.

Long-term variability in streamflow in the Red River Basin also is high. Because the basin is relatively flat and has a large surface-water and soil-moisture storage potential (Stoner and others, 1993), high or low streamflow conditions in the

Table 2. Mean daily streamflows for selected stations in the Red River of the North Basin for various periods during 1970-2001.

[--, not applicable; NT, North Dakota tributary station; MT, Minnesota tributary station; MS, main-stem station]

Site number (figure 1)	Station type	U.S. Geological Survey station number	Station name	Mean daily streamflow for 1977 (cubic feet per second)	Mean daily streamflow for 1997 (cubic feet per second)	Mean daily streamflow for 1988-92 (cubic feet per second)	Mean daily streamflow for 1995-99 (cubic feet per second)
	NT^1	05051300	Bois de Sioux River near Doran, Minnesota	10	735	71	410
	MT	05046000	Otter Tail River below Orwell Dam near Fergus Falls, Minnesota	108	754	275	670
1	MS	05051522	Red River of the North at Hickson, North Dakota	132	1,784	406	1,239
2	NT	05053000	Wild Rice River near Abercrombie, North Dakota	7.6	565	43	357
3	NT	05059000	Sheyenne River near Kindred, North Dakota	61	772	84	651
	MT	05062000	Buffalo River near Dilworth, Minnesota	44	454	88	330
	MT	05064000	Wild Rice River at Hendrum, Minnesota	56	850	179	720
4	MS	05064500	Red River of the North at Halstad, Minnesota	363	6,178	959	4,170
5	NT	05066500	Goose River at Hillsboro, North Dakota	5.4	382	39	290
6	MT	05079000	Red Lake River at Crookston, Minnesota	394	2,945	379	2,410
7	NT	05085000	Forest River at Minto, North Dakota	8.5	162	15	107
8	NT	05090000	Park River at Grafton, North Dakota	2.6	228	14	140
9	MS	05102500	Red River of the North at Emerson, Manitoba	853	13,130	1,906	9,968

¹Designated as a North Dakota tributary although the basin lies in Minnesota, North Dakota, and South Dakota.

basin can persist for years. Large moisture deficits and reduced streamflows occur during (and after) extended droughts, and moisture surpluses and increased streamflows occur during (and after) extended wet periods (Booy and Lye, 1986; Wiche and others, 2000). The extended droughts and wet periods, in

turn, can change the chemical composition of streamflow in the basin. The mean daily streamflows given in table 2 indicate the extreme long-term (5-year) variability in streamflow that can occur. The driest 5-year period was 1988-92, and the wettest 5year period was 1995-99. Streamflows for the North Dakota

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tributary stations totaled about 1,950 cubic feet per second during 1995-99 and about 270 cubic feet per second during 1988-92 for a ratio of about 7 to 1. Streamflows for the Minnesota tributary stations totaled about 4,130 cubic feet per second during 1995-99 and about 920 cubic feet per second during 1988-92 for a ratio of about 4.5 to 1. Both ratios were smaller than the corresponding ratios for the 1-year extremes (30 to 1 for the North Dakota tributary stations and 8 to 1 for the Minnesota tributary stations) because the 5-year averages smoothed some of the variability in the 1-year extremes. However, although the ratio for the 1-year extremes for the North Dakota tributary stations (30 to 1) was large in relation to the ratio for the Minnesota tributary stations (8 to 1), the ratios for the 5-year extremes for the North Dakota and Minnesota tributary stations (7 to 1 and 4.5 to 1, respectively) were comparable. Long-term variability

in precipitation and temperature was similar throughout the basin. Also, despite substantial annual (short-term) hydrologic differences between the North Dakota and Minnesota tributaries, the effect of the long-term climatic variability on streamflow in the tributaries was similar.

Concentration Data Used for Water-Quality Trend Analysis

Constituents used for the water-quality trend analysis (table 3) were chosen on the basis of data availability and the importance of the constituent concentration to aquatic health in the basin. The period of record chosen for the trend analysis was

Table 3. Constituents used for water-quality trend analysis.

Constituent	Unit	U.S. Geological Survey National Water Information System parameter code
Major ions a	and dissolved solids	
Sulfate, dissolved	Milligrams per liter	00945
Chloride, dissolved	Milligrams per liter	00940
Dissolved solids, residue at 180 degrees Celsius	Milligrams per liter	70300
ı	Nutrients	
Nitrite plus nitrate as nitrogen, dissolved	Milligrams per liter	00631
Ammonia plus organic nitrogen, total	Milligrams per liter	00625
Phosphorus, total	Milligrams per liter	00665
Tra	ace metals	
Iron, dissolved	Micrograms per liter	01046
Manganese, dissolved	Micrograms per liter	01056

the 32-year period from January 1, 1970, through December 31, 2001. This was the longest period of record for which concentration data were available for most stations.

The time-series model used for the water-quality trend analysis required a relatively long record of concentration data to evaluate the complex relation between streamflow and concentration on several time scales (annual, seasonal, and daily). Data for at least 60 samples during at least 15 years (the years

do not need to be consecutive) and at least 10 samples during each 3-month season needed to be available for each station-constituent pair selected for the trend analysis. Therefore, the available data were screened to determine which station-constituent pairs met the data requirements. The stations and constituents used are given in table 4. All of the stations met the requirements for major ions and dissolved solids, four stations met the requirements for dissolved nitrite plus nitrate as nitrogen, five stations met the requirements for total ammonia plus

 Table 4.
 Stations and constituents used for water-quality trend analysis and number of samples for concentration data.

Site		Number of Samples for							
number (figure 1)	Station name	samples for 1970-2001	1970-75	1976-80	1981-85	1986-90	1991-95	1996-2001	censored values for 1970-2001
	Major i	ons (dissolved s	sulfate and	dissolved o	hloride) an	d dissolved	d solids		
1	Red River of the North at Hickson, North Dakota	118	3	47	18	11	10	29	0
2	Wild Rice River near Abercrombie, North Dakota	151	54	50	15	10	12	10	0
3	Sheyenne River near Kindred, North Dakota	204	7	88	29	28	39	13	0
4	Red River of the North at Halstad, Minnesota	157	7	40	33	28	35	14	0
5	Goose River at Hillsboro, North Dakota	82	17	24	8	10	12	11	0
6	Red Lake River at Crookston, Minnesota	147	24	21	31	30	40	1	0
7	Forest River at Minto, North Dakota	95	25	28	9	10	11	12	0
8	Park River at Grafton, North Dakota	72	12	20	9	9	11	11	0
9	Red River of the North at Emerson, Manitoba	143	0	36	32	28	37	10	0
	Dissolved i	nitrite plus nitra	te as nitroç	jen (detecti	on limit of (0.1 milligra	m per liter)		
3	Sheyenne River near Kindred, North Dakota	180	0	85	28	27	39	1	52
4	Red River of the North at Halstad, Minnesota	106	0	17	30	24	35	0	9
6	Red Lake River at Crookston, Minnesota	117	6	10	30	30	40	1	64
9	Red River of the North at Emerson, Manitoba	122	0	16	33	26	39	8	19
	Total amı	nonia plus orga	nic nitroge	n (detectio	n limit of 0.2	2 milligram	per liter)		
1	Red River of the North at Hickson, North Dakota	92	3	47	18	3	0	21	2
3	Sheyenne River near Kindred, North Dakota	179	0	84	27	27	40	1	1
4	Red River of the North at Halstad, Minnesota	123	0	35	29	24	35	0	0

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Table 4. Stations and constituents used for water-quality trend analysis and number of samples for concentration data.—Continued

Site		Number of			Number of	f samples f	or		Percent of censored
number (figure 1)	Station name	samples for 1970-2001	1970-75	1976-80	1981-85	1986-90	1991-95	1996-2001	censored values for 1970-2001
	Total ammonia	plus organic nit	rogen (dete	ection limit	of 0.2 milliç	gram per lit	er)—Contir	nued	
6	Red Lake River at Crookston, Minnesota	131	9	22	30	29	40	1	0
9	Red River of the North at Emerson, Manitoba	140	0	34	31	28	39	8	1
		Total phosphore	ıs (detectio	on limit of O	.01 milligra	m per liter)			
1	Red River of the North at Hickson, North Dakota	91	3	47	18	3	0	20	0
3	Sheyenne River near Kindred, North Dakota	180	0	85	27	27	40	1	0
4	Red River of the North at Halstad, Minnesota	125	0	36	30	24	35	0	0
6	Red Lake River at Crookston, Minnesota	146	23	22	30	30	40	1	6
9	Red River of the North at Emerson, Manitoba	142	0	35	32	28	39	8	0
		Dissolved iron	(detection	limit of 10	micrograms	s per liter)			
3	Sheyenne River near Kindred, North Dakota	148	7	79	14	11	27	10	32
4	Red River of the North at Halstad, Minnesota	84	6	18	13	12	23	12	30
5	Goose River at Hillsboro, North Dakota	72	7	24	8	10	12	11	10
6	Red Lake River at Crookston, Minnesota	92	15	8	18	16	34	1	0
7	Forest River at Minto, North Dakota	82	15	28	9	7	11	12	21
9	Red River of the North at Emerson, Manitoba	77	0	13	17	17	22	8	35
	Di	ssolved mangan	ese (detec	tion limit of	10 microgr	ams per lit	er)		
3	Sheyenne River near Kindred, North Dakota	172	7	79	20	18	37	11	13
4	Red River of the North at Halstad, Minnesota	104	7	18	19	18	30	12	56
5	Goose River at Hillsboro, North Dakota	72	7	24	8	10	12	11	3

Table 4. Stations and constituents used for water-quality trend analysis and number of samples for concentration data.—Continued

Site				Percent of					
number (figure 1)	Station name	samples for 1970-2001	1970-75	1976-80	1981-85	1986-90	1991-95	1996-2001	- censored values for 1970-2001
	Dissolved manganese (detection limit of 10 micrograms per liter)—Continued								
6	Red Lake River at Crookston, Minnesota	100	15	8	20	19	37	1	0
7	Forest River at Minto, North Dakota	82	15	28	9	7	11	12	5
9	Red River of the North at Emerson, Manitoba	90	0	13	18	19	32	8	8

organic nitrogen and for total phosphorus, and six stations met the requirements for dissolved trace metals.

The number of censored values (values that are known to be less than the method detection limit but for which an exact value is not known) is an important consideration for trend analysis. A moderate degree of censoring can be tolerated in a timeseries analysis, but care must be taken when interpreting trend results for censored data. For this study, the method detection limit may have changed in some cases during the analysis period. Therefore, because the trend estimation technique used is not valid if the detection limit changes during the trend-analysis period or if some values are known to be less than the smallest detection limit, concentrations that were less than the highest detection limit in the record were set equal to the highest detection limit and treated as known concentrations. The degree of censoring that can be tolerated in a time-series model depends on the number and distribution of the censored values with respect to the values that exceed the detection limit. Generally, if the data, excluding the censored data, meet the requirements given previously, the model can be used for trend analysis. However, the ability to detect a water-quality trend is reduced substantially as the number of censored values increases.

For this study, the number of samples for major ions and dissolved solids was highly variable and ranged from less than 2 samples per year for some stations during various periods to more than 17 samples per year for the Sheyenne River near Kindred, N. Dak., station (site 3) during 1976-80 (table 4). During 1976-80, at least six samples per year were collected at five stations, and at least four samples per year were collected at all nine stations. The number of samples generally decreased during the 1980's and early 1990's, and, during 1996-2001, two or fewer samples per year were collected at most stations. No major-ion or dissolved-solids data were censored.

Nutrient sampling generally began in the mid- to late 1970's but was discontinued at the Kindred station (site 3), the Red River at Halstad, Minn., station (site 4), and the Red Lake River at Crookston, Minn., station (site 6) in the mid-1990's. Thus, the number of samples for nutrients also was highly variable (table 4). Except for the Red River at Hickson, N. Dak., station (site 1), the number of samples was high during 1976-95 when at least four and often six or eight samples per year were collected for most nutrients. Few samples were collected at the Hickson station (site 1) during the 1980's and early 1990's, but the station was sampled intensively during 1976-80 and during 1996-2001. Samples were collected at the Hickson station (site 1) during 1996-2001 as part of a nutrient loading study for the upper Red River (Sether and others, 2004). During that period, the Hickson station (site 1) was the only station that had a high number of samples. The percentage of censored values for dissolved nitrite plus nitrate as nitrogen was greater than 50 for the Kindred station (site 3) and the Crookston station (site 6). The percentage for total ammonia plus organic nitrogen and for total phosphorus was less than or equal to 6 for all stations.

The number of samples for dissolved trace metals generally was less than the number of samples for major ions and nutrients (table 4). Samples for dissolved iron and dissolved manganese were collected sporadically during the early 1970's and late 1990's when two or fewer samples per year were collected at most stations. For the Kindred station (site 3), the Goose River at Hillsboro, N. Dak., station (site 5), and the Forest River at Minto, N. Dak., station (site 7), the largest number of samples (more than four per year) was for 1976-80. For the remaining stations, the largest number of samples (more than four per year) was for 1991-95. The percentage of censored values for dissolved iron was greater than or equal to 30 for the Kindred station (site 3), the Halstad station (site 4), and the Red River at Emerson, Manitoba, station (site 9). The percentage for

dissolved manganese was greater than 50 for the Halstad station (site 4).

Water-Quality Trend Analysis

Time-Series Model Used for Water-Quality Trend Analysis

A statistical time-series model for streamflow and constituent concentration was used in this report to detect water-quality trends. Other applications of the model, which was developed by the U.S. Geological Survey (Vecchia, 2000), are given by Jones and Armstrong (2001), Trench and Vecchia (2002), and Vecchia (2003b). A brief description of the model is included in this section, and details on the theory and parameter estimation for the model are given in appendix 1.

The time-series model requires that no more than three water-quality samples be included in the record for any one month and that the minimum spacing between any two consecutive sampling dates is 5 days. Thus, each month of the trendanalysis period was divided into three approximately 10-day intervals—the 1st day through the 10th day of the month, the 11th day through the 20th day of the month, and the 21st day through the end of the month. The number of samples for each station and each constituent then was reduced, if necessary, so data for no more than one sampling date were used during each 10-day interval and so at least 5 days separated each pair of sampling dates. If multiple samples existed for a given 10-day interval, the sample closest to the midpoint of the interval was selected. Thus, some data given in the NWIS database were not included in the water-quality trend analysis. The number of samples given in table 4 is the (possibly) reduced number of samples. For most stations, no reduction in the number of samples was required. However, for some stations, some reduction in the number of samples was required for the late 1970's and early 1980's. The number of samples excluded from the trend analysis generally was small compared to the number of samples given in table 4.

Streamflow is an important variable in water-quality trend analyses because much of the variability in concentration is caused by variability in streamflow. Identifying and removing the streamflow-related variability in concentration increases the ability to detect trends in the presence of natural variability. Therefore, for the time-series model used in this report, each month was divided into three approximately 10-day intervals as described previously for the concentration data, and each interval was assigned a streamflow value in the following manner. If a water-quality sample was available for a given interval, the streamflow value assigned for the interval was the daily mean streamflow (hereinafter referred to as daily streamflow) for the day the water-quality sample was collected. If no water-quality

sample was available for the interval, the streamflow value assigned for the interval was the daily streamflow for the 5th, 15th, or 25th day of the month, depending on whether the interval corresponded to the beginning, middle, or end of the month. Thus, a streamflow time series that consisted of 3 values per month, or 36 values per year, was obtained for each station. In contrast to the concentration time series, which was missing values for most intervals, the streamflow time series had values for each interval for all stations included in the study. Because the time-series analysis requires a logarithmic transformation of the streamflow values to fit the model, values that were less than 0.1 cubic foot per second were set equal to 0.1.

Daily streamflows and total ammonia plus organic nitrogen and total phosphorus concentrations for the Sheyenne River near Kindred, N. Dak., station (site 3) are shown in figure 2. The daily streamflows were highly variable and ranged from about 10 to more than 5,000 cubic feet per second. Daily variability in streamflow resulted from hydroclimatic variability for various time scales that included annual (year-to-year), seasonal (month-to-month), and short-term (day-to-day) scales and occurred because daily streamflows responded to meteorological conditions, such as rainstorms or temperature patterns, that changed from day to day. Seasonal variability in streamflow was high during most years. Streamflows during the spring often were more than 100 times higher than streamflows during the fall or winter. Annual variability in streamflow also was high. The average annual streamflow during drought years (such as during 1977 and 1988-92) was about 10 times lower than the average annual streamflow during wet years (such as during 1993-2001).

The total ammonia plus organic nitrogen and total phosphorus concentrations were less variable than the daily streamflows (fig. 2). The measured concentrations generally ranged over about one order of magnitude (1 logarithmic unit), and the daily streamflows ranged over about three orders of magnitude. Although considerable variability existed in the concentrations, much of the variability could be attributed to natural streamflow-related variability. The time-series model is designed to account for as much of this natural variability as possible before detecting trends.

To detect the water-quality trends for this report, concentration data were partitioned into several components according to equation 1:

$$\log(C) = M_C + ANN_C + SEAS_C + TREND_C + HFV_C \quad (1)$$

where

log denotes the base-10 logarithm;

C is the concentration, in milligrams or micrograms per liter;

 M_C is the long-term mean of the log-transformed concentration, as the

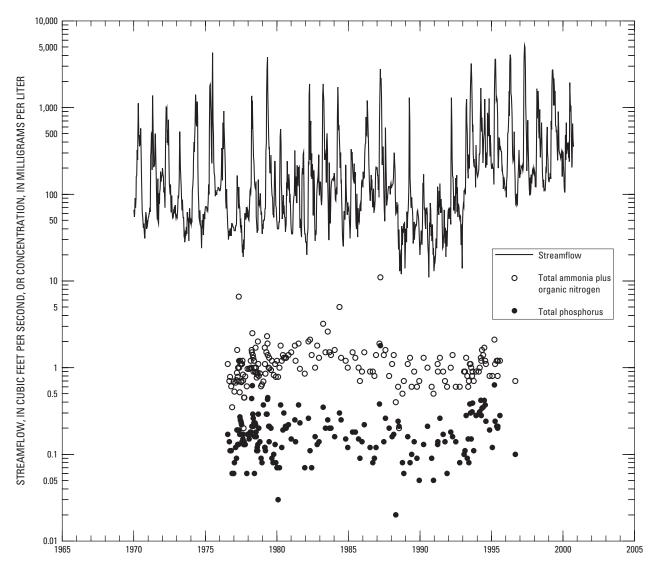


Figure 2. Daily mean streamflows (three values per month) and measured total ammonia plus organic nitrogen and total phosphorus concentrations for 1970-2001 for the Sheyenne River near Kindred, North Dakota, streamflow-gaging station.

base-10 logarithm of milligrams or micrograms per liter;

 ANN_C is the annual concentration anomaly (dimensionless);

 $SEAS_C$ is the seasonal concentration anomaly (dimensionless);

 $TREND_C$ is the concentration trend (dimensionless); and

 HFV_C is the high-frequency variability of the concentration (dimensionless).

The procedure used to partition the data is described in detail in appendix 1.

In equation 1, the annual concentration anomaly (ANN_C) , seasonal concentration anomaly $(SEAS_C)$, and high-frequency

variability (HVF_C) terms represent natural variability in concentration for different time scales. ANN_C is an estimate of the interannual variability in concentration that can be attributed to long-term variability in streamflow. Extended droughts and wet periods can change the chemical composition of streamflow by changing the degree of contact between surface runoff and soil particles and changing the relative composition of runoff among ground water, overland flow, and subsurface flow.

 $SEAS_C$ is an estimate of the seasonal variability in concentration that can be attributed to seasonal variability in streamflow or to factors other than variability in streamflow. For example, the seasonal snow-accumulation and snowmelt cycle causes seasonal fluctuations in streamflow and water quality. Seasonal temperature differences also may affect the rate of chemical processes, such as reduction of ammonia and

other nitrogen compounds to nitrate and, thus, may cause seasonal differences in nutrient concentrations. Seasonality also may occur in the sources of chemical constituents (for example, fertilizer application or roadway de-icing), independent of streamflow conditions.

 HFV_C is an estimate of the variability in concentration for time scales that are smaller than the seasonal time scale (time scales of several days to several weeks). Thus, high-frequency variability is the variability that remains after the removal of seasonal and annual anomalies and trends. Day-to-day changes in meteorological conditions may cause high-frequency variability in both streamflow and concentration. High-frequency variability also is caused by measurement error (the inability to exactly determine concentration at any given time). In contrast to the annual and seasonal concentration anomalies, which depend only on antecedent streamflow conditions, the high-frequency variability depends on a time-series model, called a periodic autoregressive moving average model, that accounts for the presence of serial correlation among concentrations (for example, the tendency for high or low values to persist for several days to several weeks before returning to normal levels).

 $TREND_C$ is an estimate of the long-term systematic changes in concentration that are unrelated to long-term variability in streamflow. A statistically significant trend might indicate changes in human activities (such as land use, fertilizer application, sewage treatment, etc.) that change the amount of a particular chemical constituent available for solution or suspension in surface water or that change the rate at which the constituent reaches the surface water. Because trends from different causes can occur at different times and in different directions, the trends described in this report are not monotonic (entirely upward or entirely downward). Rather, the trends can persist for a short time before ending or reversing direction. The number of samples collected for a constituent ultimately determines the complexity of the trend that can be detected for that constituent. For this study, a trend was defined as a statistically significant increase or decrease in median concentration for a period of 5 years or more. The methods used to detect the trends and evaluate their statistical significance are described in appendix 1.

The trend-analysis results for the data shown in figure 2 were used in this section to illustrate the concepts described previously. The fitted annual and seasonal concentration anomalies for the data are shown in figure 3. The lines in figure 3 are given by $M_C + ANN_C + SEAS_C$. The mean also is included in all subsequent concentration plots to facilitate comparison among the different stations and constituents.

The seasonal oscillations within each year (fig. 3) indicate the seasonal anomalies for total ammonia plus organic nitrogen and total phosphorus were highly variable. However, because the primary focus of this report is on the analysis of annual water-quality trends, the seasonal anomalies were treated as nuisance variability and removed from the concentration data to

facilitate comparison of the annual trends. The concentrations that have the seasonal anomaly removed, $\log(C) - SEAS_C$, are called seasonally adjusted concentrations. The seasonally adjusted concentrations are shown in figure 4 along with the fitted annual concentration anomalies, $M_C + ANN_C$.

Substantial variability occurred in the fitted annual anomalies for both constituents (fig. 4). The annual anomalies for total ammonia plus organic nitrogen ranged from about 0.8 to 1.7 milligrams per liter, and the annual anomalies for total phosphorus ranged from about 0.14 to 0.38 milligram per liter. The anomalies for total phosphorus were particularly high during 1994-96, near the onset of wet conditions that followed the drought of 1988-92 (fig. 2). However, the anomalies decreased after 1996 although streamflows remained high.

The annual anomaly for a specified year is an estimate of the median concentration that occurred for the year, given daily streamflows for the concurrent year and antecedent daily streamflows for previous years. For this report, a year is any 12-month period that ends with a specified date and does not necessarily coincide with a calendar year or water year. The annual anomaly for the given decimal year is plotted at the end of the year. For example, the largest estimated median total phosphorus concentration (about 0.38 milligram per liter) occurred for the year ending May 31, 1994 (fig. 4; decimal year 1994.5). The 1-year period from June 1, 1993, through May 31, 1994, was a very wet period that followed an extended drought.

Concentrations that have both the seasonal and annual anomalies removed are referred to in this report as standardized concentrations. Using equation 1, the standardized concentration was defined as

$$SC = \log(C) - ANN_C - SEAS_C = M_C$$
 (2)
+ $TREND_C + HFV_C$

where

SC is the standardized concentration, as the base-10 logarithm of milligrams or micrograms per liter.

The standardized concentrations defined by equation 2 are analogous to the flow-adjusted concentrations defined in previous publications as the residuals from a regression model that relates concentration to concurrent daily streamflow (Hirsch and others, 1982). However, the approach used for this report generally is more effective than a regression-based approach for removing streamflow-related variability (Vecchia, 2003a).

The standardized total ammonia plus organic nitrogen and total phosphorus concentrations for the Kindred station (site 3) are shown in figure 5 along with the fitted trends, $M_C + TREND_C$ (eq. 2), obtained as described in appendix 1. A relatively abrupt increase in the standardized concentrations

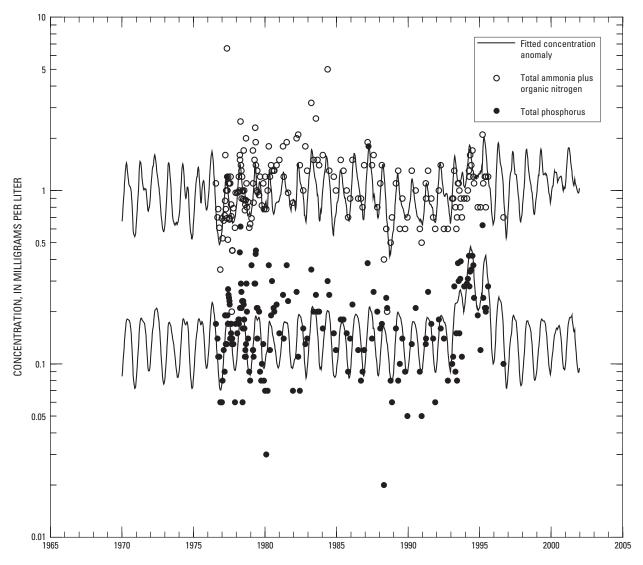


Figure 3. Measured total ammonia plus organic nitrogen and total phosphorus concentrations and fitted annual and seasonal concentration anomalies for 1970-2001 for the Sheyenne River near Kindred, North Dakota, streamflow-gaging station.

occurred during the early 1980's followed by a somewhat gradual decrease from the mid-1980's to the mid-1990's. The standardized concentrations at the end of the trend-analysis period were slightly lower than the standardized concentrations for 1976 when nutrient sampling began.

The trend in standardized concentration for a specific year (which, again, can be any 12-month period that ends with a specified date) is an estimate of the median concentration that would have occurred for the year had streamflow conditions for the year been similar to "standard" or average conditions for 1965-2001. The trends shown in figure 5 thus indicate changes in the median concentration that presumably were caused by changes in point or nonpoint sources of nitrogen or phosphorus or by changes in land use that affected the amounts of nutrients

that reached the stream. Potential changes that could affect trends in nutrient concentrations in the Red River Basin are changes in agricultural tillage practices, residential or agricultural fertilizer usage, livestock production, and industrial or municipal effluents (Tornes and Brigham, 1994). All of these changes may be subject to complex interactions and may occur at different times, in different directions, and at different rates. Potential causes for the trends will be discussed in a later section of this report.

For this example, the annual anomalies for total ammonia plus organic nitrogen and total phosphorus (fig. 4) and the fitted trends for those constituents (fig. 5) were comparable in magnitude. Therefore, to detect trends in the presence of natural variability, the natural variability needed to be removed. As indi-

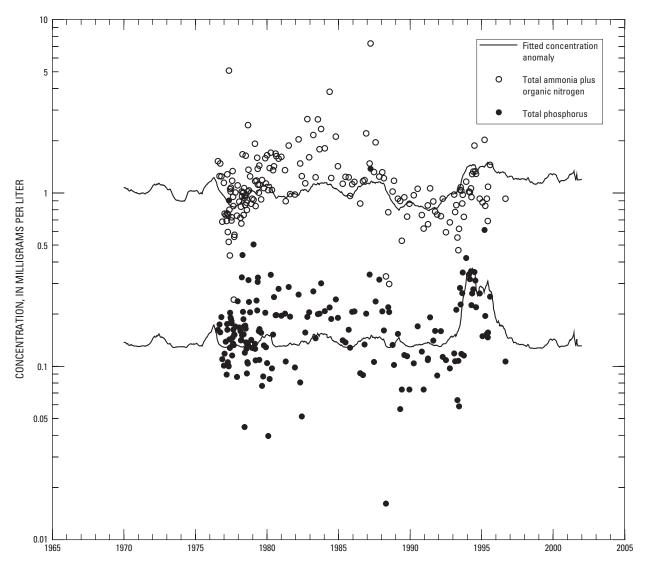


Figure 4. Seasonally adjusted total ammonia plus organic nitrogen and total phosphorus concentrations and fitted annual concentration anomalies for 1970-2001 for the Sheyenne River near Kindred, North Dakota, streamflow-gaging station.

cated in figure 4, the seasonally adjusted total phosphorus concentrations were high during the mid-1990's compared to during the rest of the trend-analysis period. However, the high concentrations were a result of the streamflow conditions that occurred at that time. As indicated in figure 5, if the streamflow conditions during the mid-1990's had been similar to those during the rest of the trend-analysis period, the median concentrations during the mid-1990's would have been lower than at any other time during the trend-analysis period.

The statistical properties for the high-frequency variability in concentration, such as the standard deviation and serial correlation, are important considerations for the determination of the statistical significance of fitted trends and for the evaluation of sampling designs. For the concentration data used in this report, the high-frequency variability was not purely random

"noise". Rather, the data generally had substantial serial correlation (the tendency for high or low values to persist from one sample to the next). Furthermore, both the standard deviation and the serial correlation depended on the time of year in which the samples were collected. For this report, the standard deviations and serial correlations were estimated as described in appendix 1. The fitted standard deviation for the total phosphorus concentration for the Kindred station (site 3) (fig. 6) indicated the standard deviation was largest for March through May and smallest for July through October. Streamflows for March through May consisted of a mixture of ground-water or reservoir discharges, rainfall or snowmelt runoff from frozen soils, and rainfall or snowmelt runoff from saturated soils, all of which had different total phosphorus concentrations and depended on the timing of the spring thaw, the amount of snow compared to rain, etc. Streamflows for July through October

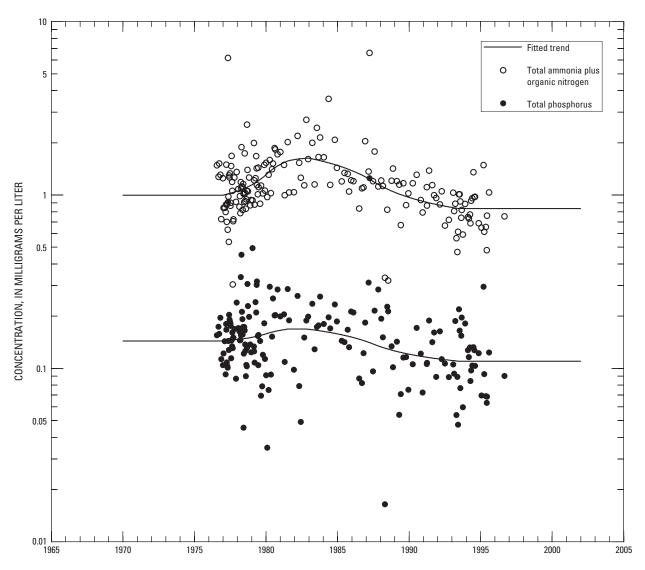


Figure 5. Standardized total ammonia plus organic nitrogen and total phosphorus concentrations and fitted trends for 1970-2001 for the Sheyenne River near Kindred, North Dakota, streamflow-gaging station.

generally consisted of ground-water or reservoir discharges, and the total phosphorus concentrations during that time had less high-frequency variability. However, because the ground-water or reservoir discharges had more serially correlated total phosphorus concentrations than the spring runoff, the serial correlation for the total phosphorus concentration was higher for July through October than for the rest of the year (fig. 6).

Results of Water-Quality Trend Analysis

The results of the water-quality trend analysis for the stations and constituents used for this study are summarized in this section. Emphasis is placed on the annual concentration anomalies, which indicate the interannual variability in concentration that can be attributed to long-term variability in streamflow, and on the trends, which indicate the long-term changes in concen-

tration that are unrelated to long-term variability in streamflow. The fitted trends are given in appendix 2 along with statistical significance levels (P-values). Unless otherwise noted, the fitted trends discussed in this section were highly significant, as indicated by a generalized likelihood ratio test with a significance level of 0.01 (see appendix 1). Thus, for any given station and constituent, the chance that the fitted trend could have occurred given the null hypothesis that the standardized concentrations were trend free was less than 1 percent (the data were trend free if their probability distribution remained the same for the entire trend-analysis period).

Major Ions and Dissolved Solids

Sulfur, although abundant in soils throughout the Red River Basin, is especially abundant in the saline soils in the

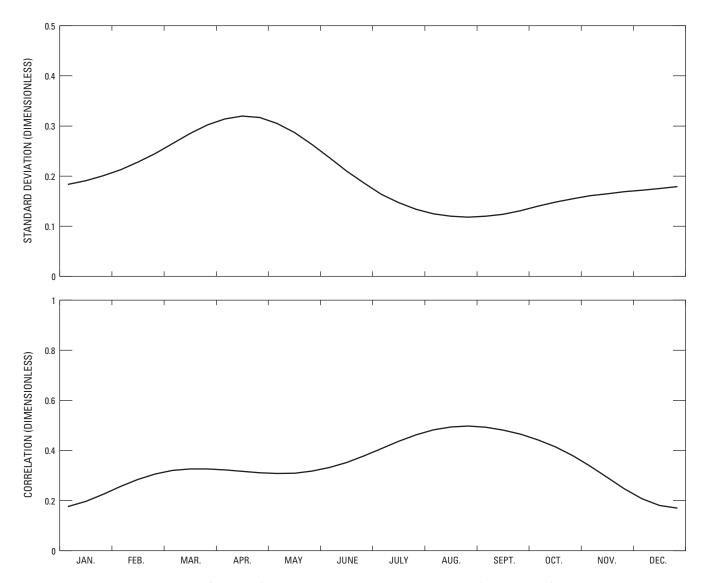


Figure 6. Fitted standard deviation (top graph) and serial correlation at a 10-day time lag (bottom graph) for the high-frequency variability in total phosphorus concentrations for the Sheyenne River near Kindred, North Dakota, streamflow-gaging station.

western part of the basin (Stoner and others, 1993). Sulfur is readily oxidized to produce sulfate ions, which, in turn, are highly soluble (Hem, 1992). Trends in dissolved sulfate concentrations may result from land-use changes, which may increase or decrease the exposure of naturally occurring sulfur to surface runoff. Human sources of sulfate, such as emissions from burning fossil fuels and wastewater discharge from mining and industrial operations, also may affect dissolved sulfate concentrations in streamflow. High dissolved sulfate concentrations have undesirable effects for drinking-water supplies and may increase the costs of municipal and rural water treatment.

Chloride, which is highly soluble, is present in soils in the Red River Basin but generally in much smaller amounts than sulfur. In contrast to other ions in streamflow (such as calcium, which bonds readily with carbon compounds), most of the chloride content of streamflow is in the form of ionized chloride (Hem, 1992). Chloride concentrations may be high in ground-water discharges from regional bedrock aquifers in the north-western part of the basin (Stoner and others, 1993; Strobel and Haffield, 1995). Human activities such as roadway and drive-way de-icing and industrial and municipal wastewater discharges may introduce chloride to streamflow.

Dissolved solids in streams in the Red River Basin are composed of calcium compounds (primarily calcium carbonate), major dissolved ions (primarily calcium, magnesium, sodium, potassium, sulfate, and chloride), and many constituents that are present in small amounts. Any of the constituents that compose the dissolved solids may cause a trend in dissolved-solids concentrations in the streams. However, trends in the individual constituents may cancel each other or, as in the

case of less abundant constituents such as dissolved nutrients and dissolved trace metals, may be too small to detect as part of a trend in dissolved-solids concentrations. Therefore, information obtained from the analysis of trends in separate constituents is more useful than that obtained from the analysis of trends in dissolved-solids concentrations.

The fitted annual concentration anomalies for dissolved sulfate for the main-stem and major tributary stations (fig. 7) indicate the anomalies for the Sheyenne River near Kindred, N. Dak., station (site 3) and the Red Lake River at Crookston, Minn., station (site 6) differed during 1988-2001. The anomalies for the Kindred station (site 3) decreased during the drought of 1988-92 and then increased to their highest levels during the wet period of 1995-2001. However, the anomalies for the Crookston station (site 6) increased during the drought and

decreased during the wet period. Although the long-term variability in streamflow for the two stations was similar (table 2), the effect of the variability on the dissolved sulfate concentrations was different. Streamflows for both stations during the drought consisted mostly of ground-water discharge, and streamflows for both stations during the wet period consisted mostly of surface runoff. Evidently, for the Kindred station (site 3), the dissolved sulfate concentrations in the ground-water discharge were lower than in the surface runoff, and, for the Crookston station (site 6), the dissolved sulfate concentrations in the ground-water discharge were higher than in the surface runoff.

The fitted annual concentration anomalies for the Red River at Hickson, N. Dak., station (site 1) were more variable than the anomalies for the remaining stations. This difference

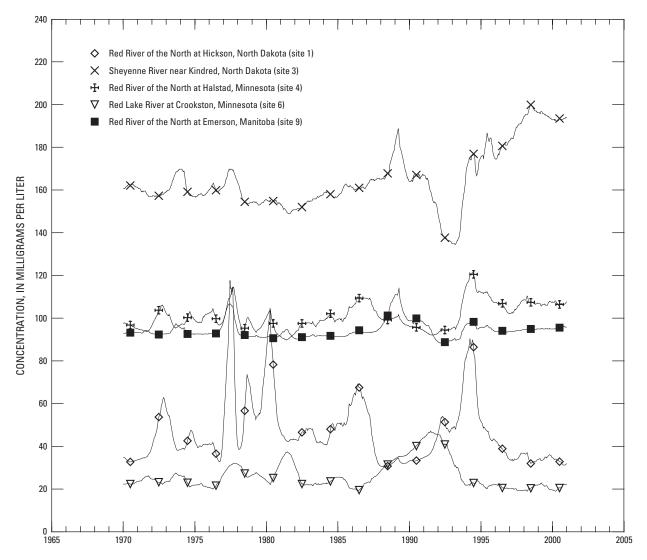


Figure 7. Fitted annual concentration anomalies for dissolved sulfate for 1970-2001 for main-stem and major tributary stations.

may be attributed to the unusual hydrologic characteristics at that site, which received streamflow from two heterogeneous basins (the Bois de Sioux and Otter Tail River Basins; fig. 1 and table 2). Although too few concentration data are available to analyze trends in dissolved sulfate for the Bois de Sioux River near Doran, Minn., station (station 05051300) and the Otter Tail River above Breckenridge, Minn., station (station 05046450), dissolved sulfate concentrations for water years 1997-99 for the Doran station (station 05051300) were much higher than those for the Breckenridge station (station 05046450). The large difference between the concentrations for the two stations along with high annual variability in streamflow (particularly for the Doran station) resulted in the high annual variability in concentrations for the Hickson station (site 1). Moreover, the anomalies for the Hickson station (site 1) often seemed to contradict the anomalies for the major tributary stations. The Red River at Halstad, Minn., received streamflow from the Red River at Hickson, N. Dak., along with streamflow from the Wild Rice River near Abercrombie, N. Dak., the Sheyenne River near Kindred, N. Dak., the Buffalo River near Dilworth, Minn., and the Wild Rice River at Hendrum, Minn. (table 2). As streamflow from those tributaries became mixed with streamflow in the Red River at Hickson, N. Dak., the variability in the concentrations for the main stem of the Red River decreased because the anomalies for the tributaries were averaged, leaving a smooth pattern of long-term variability. The Red River at Emerson, Manitoba, received streamflow from the Red Lake River at Crookston, Minn., along with streamflow from the Red River at Halstad, Minn., and many small North Dakota and Minnesota tributaries. Again, the variability in the concentrations decreased because the anomalies for the tributaries were averaged, leaving a smooth pattern of long-term variability.

The fitted annual concentration anomalies for dissolved sulfate for the small tributary stations (fig. 8) were less variable than the anomalies for some of the main-stem and major tributary stations even with the extreme interannual variability in streamflow for the small North Dakota tributaries (table 2). This apparent discrepancy probably resulted from the low number of samples (table 4) for the small North Dakota tributary stations and a large standard deviation of the high-frequency variability (eq. 1). The streamflow-related variability probably was much greater than indicated in figure 8, but additional concentration data were needed to separate the streamflow-related variability from the high-frequency variability. As indicated by this example, the ability to separate streamflow-related variability from apparent "noise", and, thus, the ability to detect concentration trends, is diminished if adequate sampling frequencies are not maintained.

The fitted trends for standardized dissolved sulfate concentrations for the main-stem and major tributary stations (fig. 9) indicate the highest median standardized concentrations for all stations occurred at the end of the trend-analysis period. During the mid-1980's and early 1990's, the median standardized concentrations increased significantly for all stations

except the Crookston station (site 6). The increase during that time was particularly large for the Red River at Emerson, Manitoba, station (site 9). Median standardized concentrations for that station during that time increased from about 65 to 115 milligrams per liter. The median standardized concentrations for the Kindred station (site 3) and the Emerson station (site 9) decreased from the late 1970's to the early 1980's. Although similar trends may have occurred during that time for the Hickson station (site 1) and the Red River at Halstad, Minn., station (site 4), no trends were detected for those stations. A small but significant trend occurred during the 1970's for the Crookston station (site 6).

The fitted trends for standardized dissolved sulfate concentrations for the small tributary stations (fig. 10) indicate particularly large trends occurred for the Wild Rice River near Abercrombie, N. Dak., station (site 2). Median standardized concentrations for that station were about 200 milligrams per liter during the early and mid-1980's and about 400 milligrams per liter during the rest of the trend-analysis period. Trends also were detected for the Forest River at Minto, N. Dak., station (site 7) and the Park River at Grafton, N. Dak., station (site 8). Median standardized concentrations for those stations increased during the mid-1980's and early 1990's. No trend was detected for the Goose River at Hillsboro, N. Dak., station (site 5). Although other trends may have occurred, none were detected because too few data are available for the small tributary stations.

The fitted annual concentration anomalies for dissolved chloride for the main-stem and major tributary stations (fig. 11) indicate the anomalies for the Hickson station (site 1) and the Crookston station (site 6) were low, irrespective of streamflow conditions. The anomalies for the Kindred station (site 3) were higher and more variable than the anomalies for the Hickson station (site 1) and the Crookston station (site 6), and the anomalies for the Halstad station (site 4) were about midway between the anomalies for the Hickson station (site 1) and the Kindred station (site 3). The anomalies for the Emerson station (site 9) were the most variable and ranged from about 20 to more than 100 milligrams per liter. The high variability for that station probably resulted from ground-water discharges from bedrock aquifers in northeastern North Dakota. The anomaly for the Emerson station (site 9) in any given year is an estimate of the median concentration for the year, and the median tended to occur during the onset of summer low-flow conditions (usually July-August). Much lower concentrations occurred during spring high-flow conditions and higher concentrations occurred during the fall and winter. During normal or wet years, tributary flows at the Emerson station (site 9) were sufficient to dilute the saline ground water during summer low-flow conditions. However, during dry years and summer low-flow conditions, the anomalies for that station increased substantially.

The fitted annual concentration anomalies for dissolved chloride for the small tributary stations (not shown) indicate the

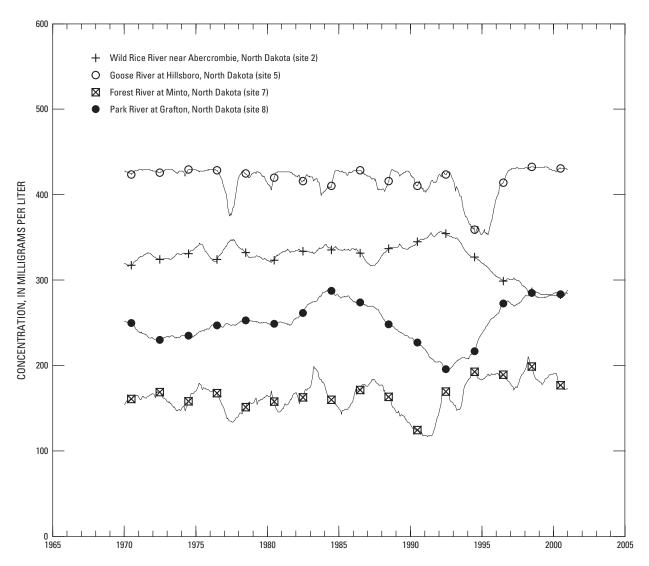


Figure 8. Fitted annual concentration anomalies for dissolved sulfate for 1970-2001 for small tributary stations.

anomalies for the Hillsboro station (site 5) and the Grafton station (site 8) were highly variable and ranged from about 30 milligrams per liter during normal or wet years to more than 160 milligrams per liter during dry years. This high variability probably resulted from ground-water discharges from bedrock aquifers in the Goose River and Park River Basins. The anomalies for the Abercrombie station (site 2) and the Minto station (site 7) were similar to those for the Kindred station (site 3) (fig. 11).

The fitted trends for standardized dissolved chloride concentrations for the main-stem and major tributary stations (fig. 12) were in general agreement with the fitted trends for standardized dissolved sulfate concentrations (fig. 9). During the mid-1980's and early 1990's, the median standardized concentrations increased significantly for all stations except the Crookston station (site 6). The increase during that time was

particularly large for the Emerson station (site 9). Median standardized concentrations for that station during that time increased from about 30 to 40 milligrams per liter. The fitted trend for standardized dissolved chloride concentrations for the Kindred station (site 3) differed somewhat from the fitted trend for standardized dissolved sulfate concentrations (fig. 9). The median standardized dissolved chloride concentrations for the Kindred station (site 3) decreased from the beginning to the end of the trend-analysis period, whereas the median standardized dissolved sulfate concentrations increased. The difference can be traced to the early 1980's, when the median standardized dissolved chloride concentrations decreased substantially more (as a percentage of the beginning concentration) than the median standardized dissolved sulfate concentrations. For all stations except the Kindred station (site 3), the highest median standardized dissolved chloride concentrations occurred at the end of the trend-analysis period.

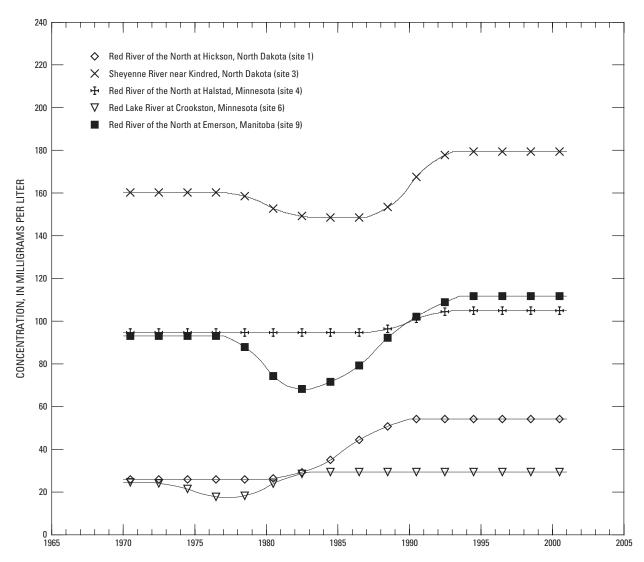


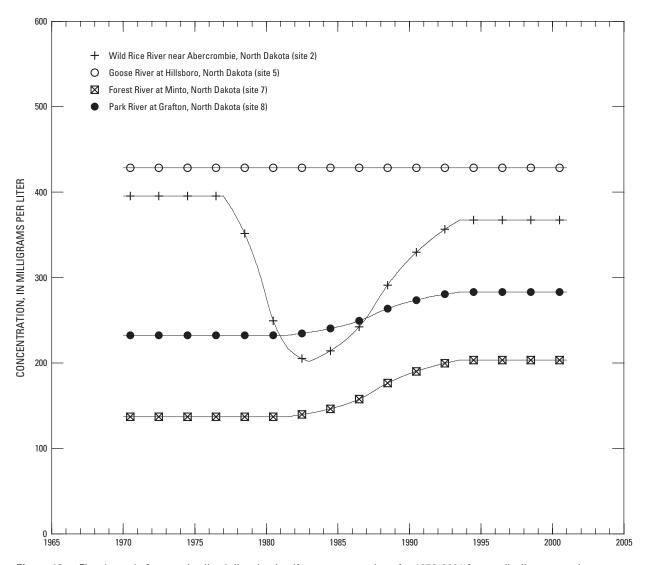
Figure 9. Fitted trends for standardized dissolved sulfate concentrations for 1970-2001 for main-stem and major tributary stations.

The fitted trends for standardized dissolved chloride concentrations for the small tributary stations (not shown) were in general agreement with the fitted trends for standardized dissolved sulfate concentrations (fig. 10). Median standardized concentrations for the Abercrombie station (site 2) were about 25 milligrams per liter during the early and mid-1980's and about 45 milligrams per liter during the rest of the trend-analysis period. The median standardized concentrations for the Grafton station (site 8) increased during the mid-1980's and early 1990's. No trends were detected for the Hillsboro station (site 5) or the Minto station (site 7).

The fitted trends for standardized dissolved-solids concentrations for the main-stem and major tributary stations (fig. 13) indicate the highest median standardized concentration for all stations occurred at the end of the trend-analysis period. A sig-

nificant increase in the median standardized concentrations occurred during the mid-1980's and early 1990's for all stations except the Crookston station (site 6). The fitted trends for standardized dissolved-solids concentrations were in general agreement with the fitted trends for standardized dissolved sulfate and dissolved chloride concentrations (figs. 9 and 12, respectively). This general agreement indicates the trends may have been caused by land-use changes that affected the amounts of naturally occurring soil compounds that reached the streams.

The fitted trends for standardized dissolved-solids concentrations for the small tributary stations (fig. 14) were in general agreement with the fitted trends for standardized dissolved sulfate concentrations (fig. 10). The only station that had no significant trend was the Hillsboro station (site 5). A significant increase in the median standardized dissolved-solids concentra-



Fitted trends for standardized dissolved sulfate concentrations for 1970-2001 for small tributary stations.

tions occurred during the mid-1980's and early 1990's for the remaining stations. Median standardized concentrations for the Minto station (site 7) and the Grafton station (site 8) increased substantially from the beginning to the end of the trend-analysis period. The median standardized concentrations increased from about 500 to 600 milligrams per liter for the Minto station (site 7) and from about 700 to 900 milligrams per liter for the Grafton station (site 8).

Nutrients

Nutrients in streamflow consist of compounds that contain nitrogen or phosphorus, which are vital for plant and animal nutrition. In contrast to major ions in streamflow, much of the nutrient content of streamflow is in the particulate, rather than the dissolved, form. Because relatively insoluble nitrogen or phosphorus compounds that are adhered to tiny suspended soil

particles or organic material often comprise a substantial part of the total nitrogen or phosphorus in the streamflow, nutrient concentrations usually are reported for both whole (unfiltered) water samples, as total concentrations, and for filtered water samples, as dissolved concentrations. Enriched nutrient concentrations in streamflow can harm the ecosystem through increased aquatic plant growth, eutrophication of lakes and streams, or increased variability in dissolved oxygen concentrations and pH (Tornes and Brigham, 1994). For this study, four stations had sufficient data to analyze trends for dissolved nitrite plus nitrate as nitrogen concentrations, and five stations had sufficient data to analyze trends for total ammonia plus organic nitrogen and total phosphorus concentrations.

Much of the dissolved nitrogen content of streamflow in the Red River Basin is in the form of nitrate ions. In the presence of oxygen, other dissolved nitrogen species (including

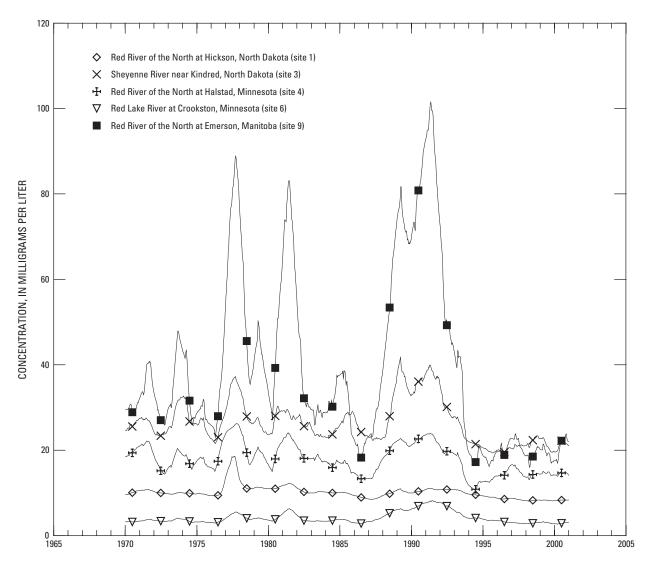


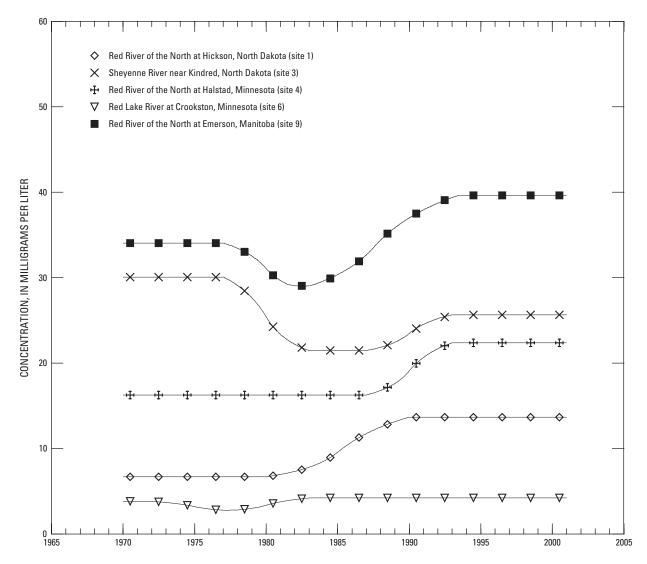
Figure 11. Fitted annual concentration anomalies for dissolved chloride for 1970-2001 for main-stem and major tributary stations.

nitrite and ammonia) easily oxidize to form nitrate, which is highly stable over a wide range of streamflow conditions (Hem, 1992). Although some of the nitrate content of streamflow is from natural sources of nitrogen in soils and the atmosphere, high nitrate concentrations often result from human activities such as industrial effluent, livestock production, fertilizer application, and sewage disposal. Changes in any of these human activities may cause trends in dissolved nitrite plus nitrate concentrations. High dissolved nitrite plus nitrate concentrations in drinking water can have undesirable health effects.

Total ammonia plus organic nitrogen, also called Kjeldahl nitrogen, represents the total of both ammonia and organic nitrogen. However, because ammonia is readily converted to nitrate, generally only a small percentage of the constituent is in the ammonia form. Most of the total nitrogen content of stream-

flow in the Red River Basin is in the form of organic nitrogen or dissolved nitrate. Because organic nitrogen adheres to the fine-grained soils in the Red River Basin, organic nitrogen concentrations in streamflow are not particularly high compared to those in other regions of the country (Stoner and others, 1993). However, human activities can increase the susceptibility of soil to erosion and increase the amount of organic nitrogen that reaches streamflow. Animal waste and fertilizer application also may be substantial sources of organic nitrogen in streamflow (Tornes and Brigham, 1994).

Although phosphorus is a common naturally occurring element in soils, the low solubility of most phosphorus compounds results in relatively low phosphorus concentrations in streamflow in relation to nitrogen concentrations in streamflow (Hem, 1992). However, because phosphorus is essential to plant and



Fitted trends for standarized dissolved chloride concentrations for 1970-2001 for main-stem and major tributary Figure 12. stations.

animal metabolism, even low concentrations can cause an increase in aquatic plant growth and have an adverse effect on water quality. Thus, maintaining low total phosphorus concentrations in streamflow is a primary concern for water quality. Potential sources of phosphorus in streamflow in the Red River Basin include soil erosion, animal waste, fertilizer application, and industrial and municipal wastewater discharge (Tornes and Brigham, 1994).

The fitted annual concentration anomalies for dissolved nitrite plus nitrate as nitrogen (fig. 15) were more variable for the Sheyenne River near Kindred, N. Dak., station (site 3) than for the Red Lake River at Crookston, Minn., station (site 6). The anomalies for the Kindred station (site 3) ranged from about 0.15 to 0.5 milligram per liter, and the anomalies for the Crookston station (site 6) were constant at about 0.15 milligram per

liter. Interannual variability in streamflow was high for both stations. However, either the variability in streamflow did not affect the anomalies for the Crookston station (site 6) or the variability was not detected because of the high percentage of censored values for that station (table 4). The anomalies for the Red River at Halstad, Minn., station (site 4), which had a small percentage of censored values, generally were much higher than the anomalies for the Kindred station (site 3) and the Crookston station (site 6) except during 1994-96 when the anomalies for the Kindred station (site 3) were high. Substantial streamflowrelated variability was detected for the Halstad station (site 4), and the anomalies for that station ranged from about 0.2 to 0.45 milligram per liter. The high anomalies for the Halstad station (site 4) indicate a substantial source of nitrate existed in the Red River at Halstad, N. Dak., Basin. However, the generally lower anomalies for the Kindred station (site 3) indicate the

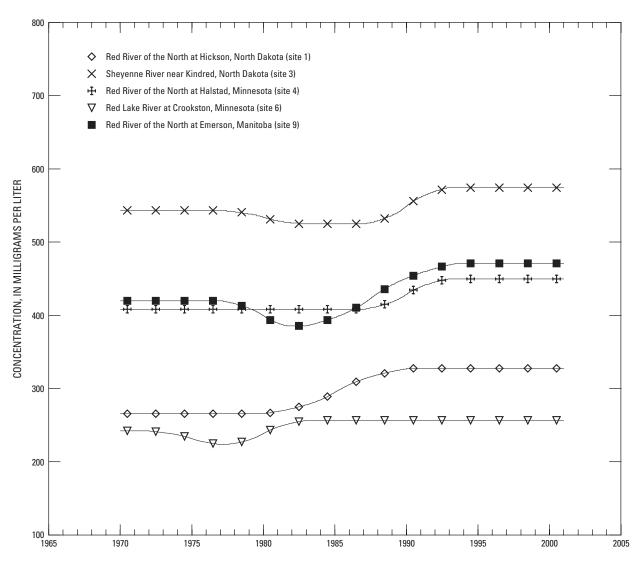


Figure 13. Fitted trends for standardized dissolved-solids concentrations for 1970-2001 for main-stem and major tributary stations.

Sheyenne River near Kindred, N. Dak., probably was not the primary source of the dissolved nitrite plus nitrate as nitrogen, and the similarity between the measured concentrations for the Red River at Hickson, N. Dak., station (site 1) for the late 1970's and early 1980's (not shown) and the measured concentrations for the Kindred station (site 3) indicates the Red River at Hickson, N. Dak., also probably was not the primary source of the dissolved nitrite plus nitrate as nitrogen. Therefore, the large amount of nitrate probably came from one of the intermediate tributaries (table 2), from point sources of nitrate in the Fargo-Moorhead area (fig. 1), or from a combination of both tributary and point sources as indicated by the pattern of variability for the Halstad station (site 4). Additional data for the tributaries are needed to determine a definitive cause for the high dissolved nitrite plus nitrate as nitrogen concentrations. The anomalies for the Red River at Emerson, Manitoba, station

(site 9) generally were less than those for the Halstad station (site 4) and the pattern of variability in the anomalies for the Emerson station (site 9) was similar to the pattern for the Halstad station (site 4). Therefore, the tributary and point sources of nitrate that are downstream from the Halstad station (site 4) probably did not affect the nitrate concentrations for the Emerson station (site 9) as much as the sources that are upstream from the Halstad station (site 4).

The fitted trends for standardized dissolved nitrite plus nitrate as nitrogen concentrations (fig. 16) indicate highly significant increases in the median standardized concentrations occurred from the mid-1980's to the mid-1990's for the Halstad station (site 4) and the Emerson station (site 9). The median standardized concentrations for the Kindred station (site 3) decreased from the early 1980's to the mid-1990's and were

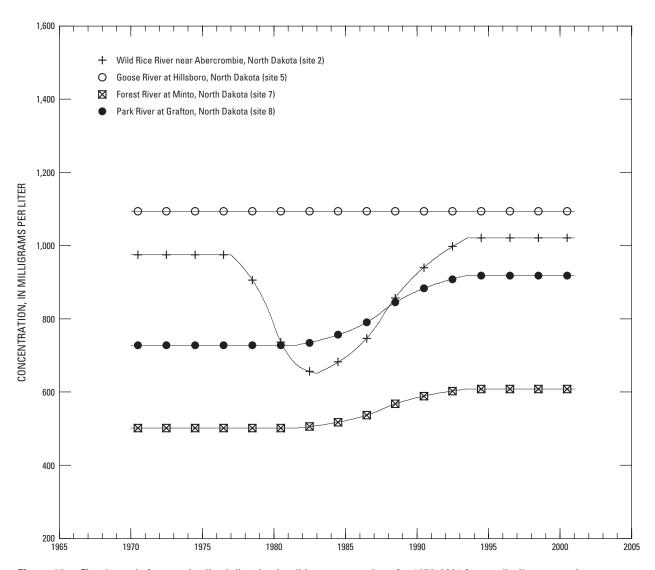


Figure 14. Fitted trends for standardized dissolved-solids concentrations for 1970-2001 for small tributary stations.

nearly stable for the Crookston station (site 6). The increasing concentrations for the main-stem stations along with the decreasing or nearly stable concentrations for the tributary stations indicate the upward trends for the Halstad station (site 4) and the Emerson station (site 9) may have been caused by human activities along the main stem of the Red River. The significant downward trend for the Kindred station (site 3) and the small but insignificant downward trend for the Crookston station (site 6) probably were not affected by the high percentage of censored values for those stations because, although censored values can make trends more difficult to detect than if all the concentrations are known, the censored values should not cause a downward trend to be detected when an upward trend exists in the uncensored data.

The fitted annual concentration anomalies for total ammonia plus organic nitrogen (not shown) indicate the anomalies

were relatively uniform among stations when compared to the anomalies for other constituents. The anomalies ranged from about 0.7 to 0.9 milligram per liter for the Hickson station (site 1), 0.8 to 1.5 milligrams per liter for the Kindred station (site 3), 1.0 to 1.5 milligrams per liter for the Halstad station (site 4), 0.9 to 1.2 milligrams per liter for the Crookston station (site 6), and 1.0 to 1.3 milligrams per liter for the Emerson station (site 9). The relatively uniform anomalies may indicate the sources of organic nitrogen are distributed evenly among the basins.

Significant trends for standardized total ammonia plus organic nitrogen concentrations occurred for all stations except the Crookston station (site 6) (fig. 17). The fitted trends for the Kindred station (site 3), the Halstad station (site 4), and the Emerson station (site 9) were in close agreement. Median standardized concentrations for those stations increased from the late 1970's to the early 1980's and then decreased from the

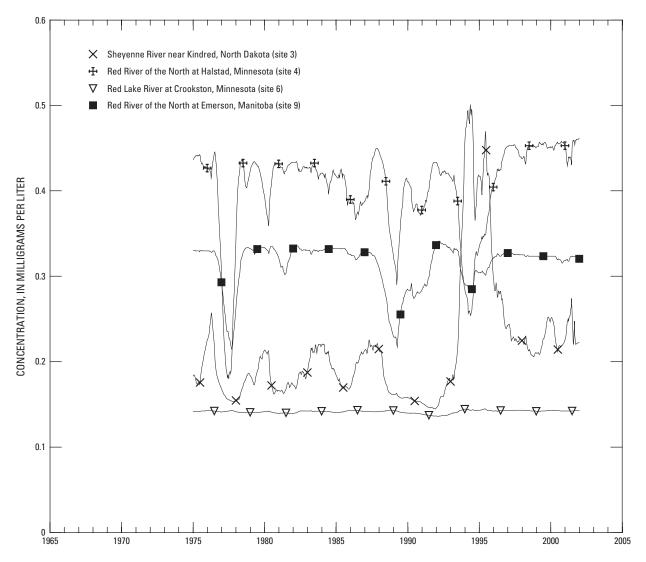
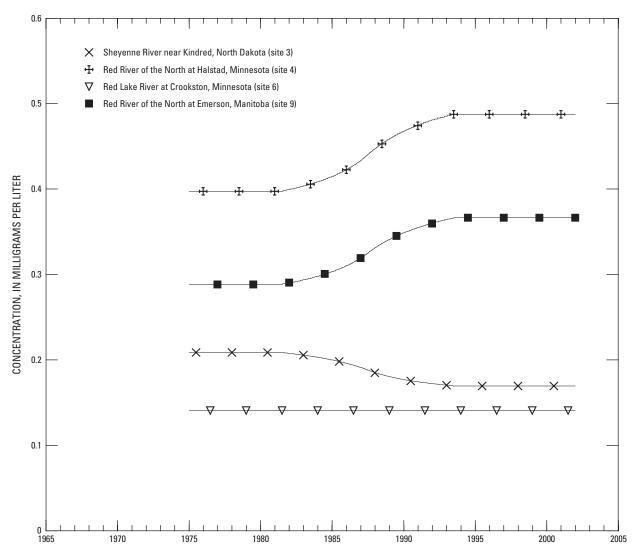


Figure 15. Fitted annual concentration anomalies for dissolved nitrite plus nitrate as nitrogen for 1975-2001.

early 1980's to the mid-1990's. A highly significant decrease in the median standardized concentrations occurred from the early 1980's to the mid-1990's for the Hickson station (site 1), but no earlier trend was detected for that station. For all stations except the Crookston station (site 6), the lowest median standardized concentrations occurred at the end of the trend-analysis period.

The fitted annual concentration anomalies for total phosphorus (fig. 18) indicate the anomalies for the Hickson station (site 1) and the Crookston station (site 6) were relatively constant during the trend-analysis period. The insensitivity of the anomalies to annual streamflow conditions may indicate soil erosion and point sources of phosphorus were not major factors in those basins. The anomalies for the Kindred station (site 3) were similar to the anomalies for the Hickson station (site 1) except during the mid-1990's when the anomalies for the Kindred station (site 3) increased to about 0.3 milligram per liter.

The anomalies for the Halstad station (site 4) tended to be considerably higher than the anomalies for the Hickson station (site 1) and the Kindred station (site 3), particularly during dry years such as 1977 and 1988-92. The high anomalies for the Halstad station (site 4) may reflect contributions from point sources of phosphorus in the Fargo-Moorhead area or from other intervening drainage areas. The anomalies for the Emerson station (site 9) were between the anomalies for the Halstad station (site 4) and the Crookston station (site 6), and the pattern of variability for the Emerson station (site 9) was similar to the pattern for the Halstad station (site 4). During 1995-2000 (the wettest 5-year period analyzed), median total phosphorus concentrations for the Halstad station (site 4) and the Emerson station (site 9) were lower than at any other time during 1970-2001 because of generally low total phosphorus concentrations for tributary flows and dilution of contributions from point sources of total phosphorus.



Fitted trends for standardized dissolved nitrite plus nitrate as nitrogen concentrations for 1975-2001.

The fitted trends for standardized total phosphorus concentrations for the Kindred station (site 3) increased from the late 1970's to the early 1980's and decreased from the early 1980's to the mid-1990's (fig. 19). The fitted trends for the Crookston station (site 6) also decreased from the early 1980's to the mid-1990's. The lowest median standardized concentrations for the Kindred station (site 3) and the Crookston station (site 6) occurred at the end of the trend-analysis period. Small but insignificant increases in the median standardized concentrations occurred for the Halstad station (site 4) and the Emerson station (site 9), and both stations had a high number of samples during the trend-analysis period (table 4). Therefore, the downward trends for the Kindred station (site 3) and the Crookston station (site 6) probably were offset by contributions from point sources of phosphorus along the main stem of the Red River or by increased total phosphorus concentrations for some of the intermediate tributaries.

Trace Metals

Trace-metal concentrations in streamflow in the Red River Basin are much lower than dissolved major-ion concentrations in streamflow in the basin. The trace metals in streamflow exist in both the dissolved and particulate form, but only the dissolved concentrations were included in this report because few whole-water concentrations were available. The concentrations of most trace metals in the basin were below detection limits, but the concentrations for the trace metals included in this report (dissolved iron and dissolved manganese) routinely exceeded detection limits. Because of the relatively small number of samples, the high noise in laboratory determinations, and the complex effects of pH, temperature, and other physical properties on chemical reactions, detecting and interpreting trends in trace elements for this report was particularly challenging.

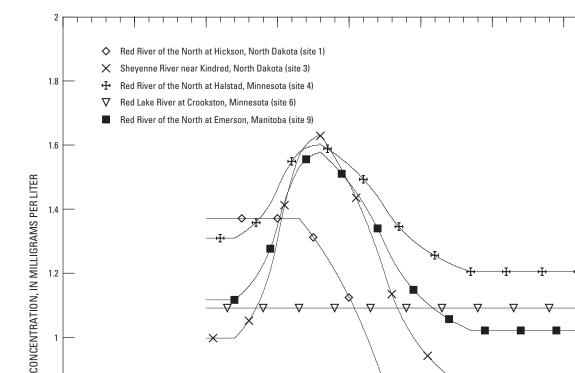


Figure 17. Fitted trends for standardized total ammonia plus organic nitrogen concentrations for 1975-2001.

1985

1990

1980

Iron is an abundant element in soils throughout the Red River Basin and elsewhere. However, because iron is not highly soluble, dissolved iron concentrations in streamflow in the basin generally are low. The dissolved iron concentrations are dependent on physical properties (pH, temperature, etc.) and on the activity of micro-organisms that affect the oxidation and reduction of iron (Hem, 1992). Iron can be introduced to streamflow through human activities such as fertilizer application, mining, and industrial effluent. Land-use changes also can increase or decrease the amount of iron that reaches streamflow. Although iron is essential for plant and animal life, high concentrations in streamflow can cause undesirable health effects. In contrast to the dissolved iron concentrations in surface runoff in the basin, the dissolved iron concentrations in ground water may be high. The dissolved iron concentrations in glacial-drift aquifers in the basin commonly exceed 300 micrograms per liter (Stoner and others, 1993).

1970

1975

0.8

0.6

0.4 **-**1965

As with dissolved iron, dissolved manganese concentrations in streamflow are highly dependent on physical properties (pH, temperature, etc.) and on the activity of micro-organisms that affect the oxidation and reduction of manganese (Hem, 1992). Manganese can be introduced to streamflow through human activities such as mining and industrial effluent. Changes in cultivation practices or other farming activities also can increase or decrease the amount of manganese that reaches streamflow. Although manganese is essential for plant and animal life, high concentrations in streamflow can cause undesirable health effects.

1995

2000

2005

The fitted annual concentration anomalies for dissolved iron (not shown) indicate no discernible patterns of variability. The anomalies were highest for the Goose River at Hillsboro, N. Dak., station (site 5) and ranged from about 20 to 60 micrograms per liter for that station. The anomalies for the

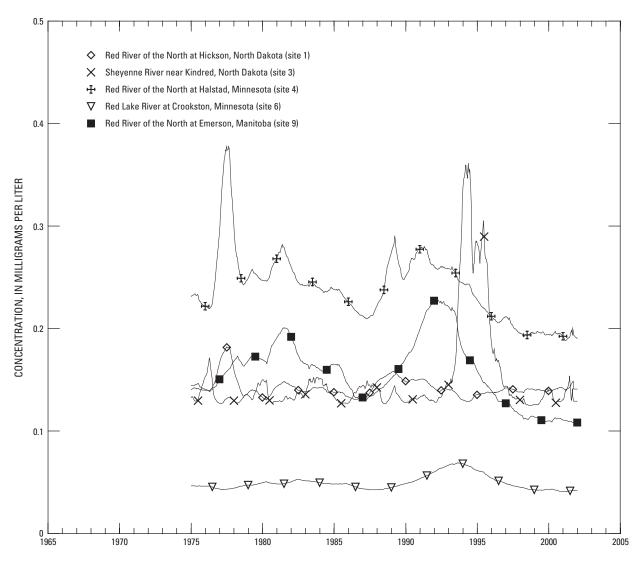


Figure 18. Fitted annual concentration anomalies for total phosphorus for 1975-2001.

remaining stations were similar and ranged from about 10 to 40 micrograms per liter. The lack of a consistent pattern in the annual anomalies may indicate the variability was caused by complex chemical processes rather than by streamflow. Alternatively, the combination of extreme high-frequency variability, few data, and the number of censored values may have disguised the streamflow-related variability.

No trends were detected for standardized dissolved iron concentrations. A large decrease in the median standardized concentrations occurred in the late 1970's for all stations, but the decrease was deemed too large and abrupt to indicate a real trend. Although no documented changes in sampling or laboratory methods were noted for that period, the decrease may have been related to rounding errors or to changes in the accuracy of reported concentrations. Although no significant trends were detected for 1980-2001, small but insignificant increases in the

median standardized concentrations occurred during that time for all stations except the Hillsboro station (site 5). The coincidence of the trends, despite the small number of samples and the number of censored values, may indicate dissolved iron concentrations increased during the 1980's and 1990's.

The fitted annual concentration anomalies for dissolved manganese (fig. 20) indicate the anomalies for the Red River at Halstad, Minn., station (site 4), the Red Lake River at Crookston, Minn., station (site 6), and the Red River at Emerson, Manitoba, station (site 9) were low (less than 20 micrograms per liter) for the entire trend-analysis period. The anomalies for the Sheyenne River near Kindred, N. Dak., station (site 3) and the Forest River at Minto, N. Dak., station (site 7) were higher and more variable than the anomalies for the Halstad station (site 4), the Crookston station (site 6), and the Emerson station (site 9). The anomalies ranged from about 30 to 80 micrograms

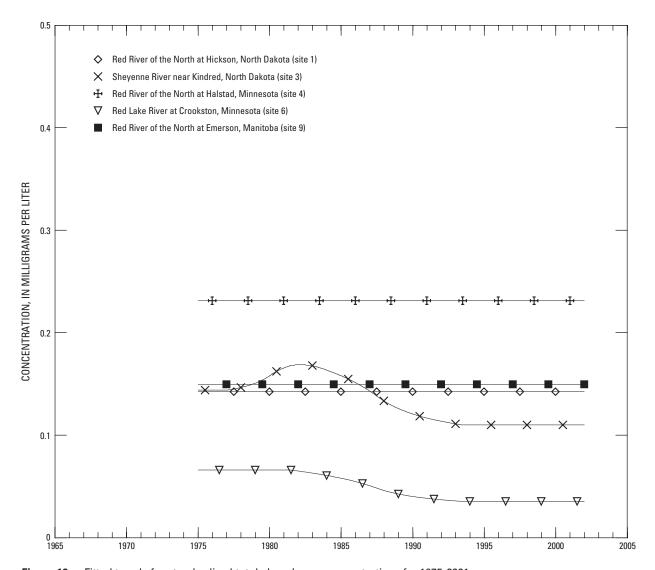


Figure 19. Fitted trends for standardized total phosphorus concentrations for 1975-2001.

per liter for the Kindred station (site 3) and from about 80 to 160 micrograms per liter for the Minto station (site 7). The anomalies for the Hillsboro station (site 5) were the most variable and ranged from about 100 to 700 micrograms per liter. During dry conditions, the anomalies for that station increased dramatically, probably as a result of high manganese concentrations in ground-water discharges. During wet conditions, such as during 1995-2001, the anomalies were similar to those for the Minto station (site 7).

As with dissolved iron, no trends were detected for standardized dissolved manganese concentrations. However, in contrast to dissolved iron, no noticeable decreases occurred in the median standardized concentrations during the late 1970's, and no consistent pattern (either increasing or decreasing) occurred in the fitted trends for the 1980's or 1990's.

Possible Human Causes of Historical Water-Quality Trends

Trend-analysis results for this study indicate significant changes that could not be attributed to natural streamflow-related variability occurred in the dissolved ion and nutrient concentrations in the Red River Basin during 1970-2001. Therefore, in this section, changes in water quality in the basin in relation to human activities are explored. The fitted trends are compared to known changes in human activities during 1970-2001 to identify which changes probably were related to the fitted trends and which changes probably were not related to the fitted trends. A full analysis of cause and effect would require a dynamic source-and-transport watershed model and was beyond the scope of this study.

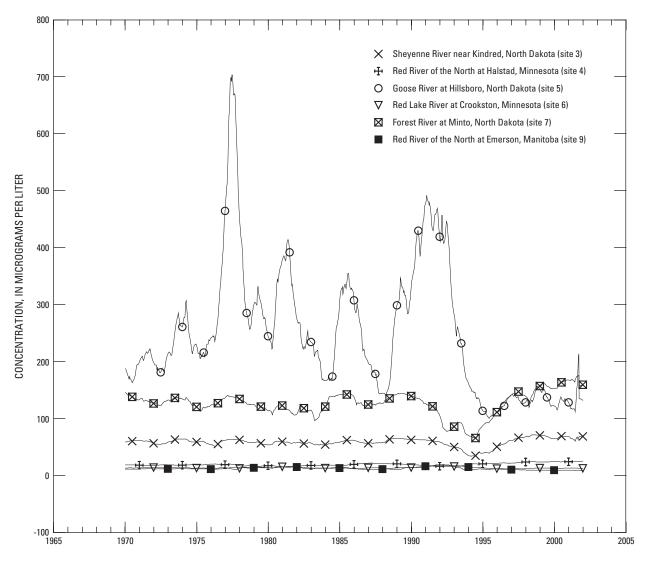


Figure 20. Fitted annual concentration anomalies for dissolved manganese for 1970-2001.

Also, the exploration of potential causes of historical water-quality trends specific to small basins was not feasible given the limits of this study. Therefore, only potential causes for the trends for the main-stem and major tributary stations were considered in this section. To further limit the scope, only trends in nutrients will be discussed. The trend results for nutrients indicate standardized dissolved nitrite plus nitrate as nitrogen concentrations for the main-stem stations increased from the early 1980's to the mid-1990's, but standardized dissolved nitrite plus nitrate as nitrogen concentrations for the major tributary stations decreased or remained stable during that time (fig. 16). The standardized total ammonia plus organic nitrogen concentrations increased from the late 1970's to the early 1980's for the Sheyenne River near Kindred, N. Dak., station (site 3), the Red River at Halstad, Minn., station (site 4), and the Red River at Emerson, Manitoba, station (site 9), but no trends were detected for the remaining stations during that time

(fig. 17). From the early or mid-1980's to the mid-1990's, the standardized total ammonia plus organic nitrogen concentrations decreased for all stations except the Red Lake River at Crookston, Minn., station (site 6). The standardized total phosphorus concentrations for the Kindred station (site 3) and the Crookston station (site 6) decreased from the early 1980's to the mid-1990's, but no trends were detected for the main-stem stations during that time (fig. 19).

Demographic and land-use changes are primary considerations for a trend analysis. The 1990 population of the study area for this report was 511,000 (Stoner and others, 1993). About 220,000 people lived in communities or cities that had populations of more than 3,000, and about 291,000 people lived in rural areas or small communities. Major urban areas in the study area are the Fargo, N. Dak.-Moorhead, Minn., area, which had a 1990 population of about 106,000, and the Grand

Forks, N. Dak.-East Grand Forks, Minn., area, which had a 1990 population of about 58,000 (fig. 1). Both the size and distribution of the population changed little during most of the trend-analysis period. Although a small (about 8 percent) increase in population occurred from 1980 to 1990, most of the growth during 1970-2001 occurred in the Fargo-Moorhead area and started in the mid-1990's. Therefore, although population changes may have affected water quality late in the trend-analysis period, the nutrient trends described in this report probably were not related to population growth.

Agriculture is the predominant land use in the Red River Basin. About 74 percent of the land area is agricultural (mostly cropland), and the remainder consists of forests and woodlands (12 percent), water and wetlands (4 percent), urban areas (3 percent), and small areas that have various land uses (Stoner and others, 1993). Most of the forests, woodlands, and wetlands are located in the eastern one-third of the basin (Stoner and others, 1993), and the Crookston station (site 6) is the only station for which most of the drainage area consists of forests and wetlands. Therefore, except for a small decrease in the total phosphorus concentration, the lack of significant trends in nutrient concentrations for the Crookston station (site 6) may indicate changes in agriculture caused some of the trends for the remaining stations. Agricultural sources of nutrients, including fertilizer applications and livestock wastes, supply much of the total nitrogen input for the study area (Tornes and Brigham, 1994; Smith and Alexander, 2000).

Cropland data for all Minnesota, North Dakota, and South Dakota counties that overlap the study area (U.S. Department of Agriculture, National Agricultural Statistics Service, accessed June 25, 2002) were used to compute a time series of total cropland for 1974-2001 for various crop groups (fig. 21). Most of the cropland in the basin was planted in wheat, barley, oats, soybeans, corn, and sunflowers. Other major crops produced in parts of the basin included flax (mostly in the northwestern part of the basin), potatoes (mostly in the central and north-central parts of the basin), and sugar beets (mostly in the southern and central parts of the basin). Major changes in the amount and distribution of cropland during the trend-analysis period are shown in figure 21. Total cropland increased by about 1 million acres during the late 1970's. Although the increase was only about 9 percent of the total cropland in 1975, most of the increase occurred in the western counties where about 1 million acres of new cropland was planted primarily in sunflowers and about 0.5 million acres of cropland was converted from wheat acreage to sunflower acreage. The timing and expected effect of this change are consistent with the increased total ammonia plus organic nitrogen concentrations that occurred during the late 1970's for the Kindred station (site 3), the Halstad station (site 4), and the Emerson station (site 9) (fig. 17). The conversion of grassland and wheat acreage to sunflower acreage may have resulted in increased mobilization of organic nitrogen in soils or increased application of nitrogen fertilizer to soils.

Other major cropland changes that occurred during the late 1970's consisted of a decrease of about 1 million acres of wheat in the southern counties and an offsetting increase of about 1 million acres of soybeans. Soybeans are nitrogen fixing and, in contrast to wheat, do not require nitrogen fertilizer. However, whether soybeans would increase or decrease the mobilization of organic nitrogen in soils is unknown. The Red River at Hickson, N. Dak., station (site 1) would be most likely to show the effect of land-use changes in the southern counties, and no trend in total ammonia plus organic nitrogen concentrations was detected for that station during the late 1970's (fig. 17).

During the early 1980's, the changes that occurred in the western counties during the late 1970's essentially were reversed—sunflower acreage decreased by about 1.5 million acres, wheat acreage increased by about 0.5 million acres, and total cropland decreased by about 1 million acres. The trends in the total ammonia plus organic nitrogen concentrations for the Kindred station (site 3), the Halstad station (site 4), and the Emerson station (site 9) reversed as well (fig. 17).

From the mid-1980's through the end of the trend-analysis period, total cropland remained stable, but wheat acreage decreased and soybean acreage increased. The change from wheat acreage to soybean acreage was widespread but was most prevalent in the southern and central parts of the basin. In 2001, the number of acres planted to wheat was about 3 million acres less than in 1975 and the number of acres planted to soybeans was about 3 million acres more than in 1975. The resulting decrease in the application of nitrogen fertilizer to soils may have contributed to the decrease in total ammonia plus organic nitrogen concentrations during the mid-1980's and early 1990's. Improvements in conservation tillage practices also may have contributed to the decrease in total ammonia plus organic nitrogen concentrations during that time.

Livestock data for all Minnesota, North Dakota, and South Dakota counties that overlap the study area (U.S. Department of Agriculture, National Agricultural Statistics Service, accessed June 25, 2002) were used to compute a time series of total livestock inventories for 1974-2001 (fig. 22). Total livestock production in the Red River Basin generally decreased during the trend-analysis period. The total livestock inventory (cattle, hogs, and sheep) decreased by about 0.8 million head from 1975 to 2001. Most of the decrease was in cattle. The decrease was widespread throughout the basin and would be expected to have a similar effect on nutrient concentrations for all stations. However, total ammonia plus organic nitrogen concentrations for the Halstad station (site 4) and the Emerson station (site 9) for 2001 were similar to the concentrations for 1975 (fig. 17). Therefore, either the decrease in livestock production had little effect on organic nitrogen concentrations or the effect was offset. For example, if confined feeding operations increased along the main stem of the Red River, the amount of organic nitrogen that reached the main stem also may have increased.

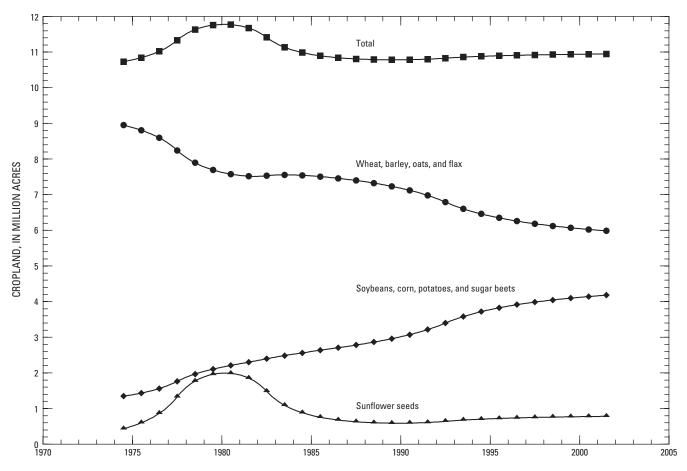


Figure 21. Estimated cropland for the Red River of the North at Emerson, Manitoba, Basin for 1974-2001. (Smoothed curves fitted to cropland data from the U.S. Department of Agriculture, National Agricultural Statistics Service, accessed June 25, 2002.)

The contrast between the fitted trends for the standardized dissolved nitrite plus nitrate as nitrogen concentrations (fig. 16) and the standardized total ammonia plus organic nitrogen concentrations (fig. 17) may indicate the increases in dissolved nitrite plus nitrate as nitrogen concentrations were caused by something other than changes in cropland because changes in cropland generally would affect both constituents in a similar manner. Although nitrogen inputs from fertilizer may percolate though the soil and cause increases in nitrate concentrations in ground water, the nearly 10-year lag between the upward trends for dissolved nitrite plus nitrate as nitrogen and the upward trends for total ammonia plus organic nitrogen probably rules out a connection between the trends for the two constituents. The upward trends in dissolved nitrite plus nitrate as nitrogen concentrations also contrast with the downward trends in livestock inventories. However, if confined feeding operations increased along the main stem of the Red River, the amount of nitrate in ground water also may have increased. Only three counties in the study area had an increase in livestock inventories during the 1980's and 1990's, and all three were Minnesota counties that are located within the drainage basin of the Red River at Hickson, N. Dak. Dissolved nitrite plus nitrate as nitrogen concentrations for the Hickson station (site 1) were not available after 1985. However, total nitrite plus nitrate concentrations (which are comparable to dissolved concentrations) were available for that station, and the number of samples was similar to the number for total ammonia plus organic nitrogen (table 4). A trend analysis of the total nitrite plus nitrate concentrations indicated a small but insignificant decrease in standardized total nitrite plus nitrate concentrations occurred from the early 1980's to the mid-1990's. Therefore, an increase in confined livestock operations along the main stem of the Red River probably did not cause the increase in dissolved nitrite plus nitrate as nitrogen concentrations.

The discussion in the previous paragraph indicates the standardized dissolved nitrite plus nitrate as nitrogen concentrations for the Halstad station (site 4) (fig. 16) probably increased downstream from the Hickson station (site 1) and the higher concentrations probably were not caused by changes in cropland or livestock-related activities. Although a definitive cause for the increase cannot be determined without additional data, the increase may have been related to municipal wastewater discharges, urban runoff, or industrial sources in the Fargo-Moor-

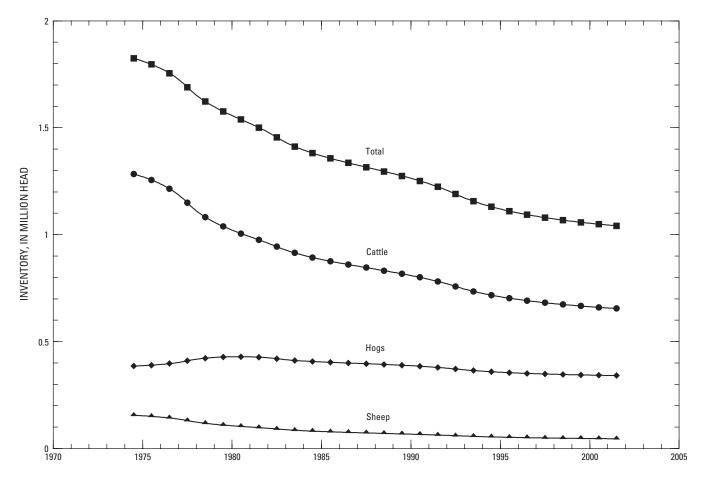


Figure 22. Estimated livestock inventory for the Red River of the North at Emerson, Manitoba, Basin for 1974-2001. (Smoothed curves fitted to cropland data from the U.S. Department of Agriculture, National Agricultural Statistics Service, accessed June 25, 2002.)

head area. The nearly equal increase in standardized concentrations for the Halstad station (site 4) and the Emerson station (site 9) (fig. 16) indicates dilution downstream from Halstad (primarily from the Red Lake River) did not reduce the magnitude of the trend as might be expected if no point sources were located downstream from Halstad. Therefore, municipal or industrial sources in the Grand Forks-East Grand Forks area also may have contributed to the higher dissolved nitrite plus nitrate as nitrogen concentrations in the main stem.

The similarity between the fitted trends for standardized total ammonia plus organic nitrogen concentrations (fig. 17) and standardized total phosphorus concentrations (fig. 19) for the Kindred station (site 3) may indicate changes in cropland or livestock-related activities caused both trends. The downward trend in standardized total phosphorus concentrations for the Crookston station (site 6) may be related to changes in livestock-related activities. Slight decreases in livestock inventories occurred in the eastern Red Lake River Basin (east of 95.5 degrees longitude; fig. 1), and large decreases in livestock inventories occurred in other parts of the basin.

No significant trends were detected in standardized total phosphorus concentrations for the main-stem stations (fig. 19). However, small but insignificant increases in the standardized concentrations were detected for the Halstad station (site 4) and the Emerson station (site 9). The previous discussion indicates changes in cropland or livestock-related activities probably would cause a decrease in total phosphorus concentrations. An improvement in wastewater-treatment practices from the 1970's to the mid-1990's (Litke, 1999) also probably would cause a decrease in total phosphorus concentrations in municipal wastewater discharges. Phosphorus concentrations may have increased from urban runoff or industrial sources in the Fargo-Moorhead area or from other sources along the main stem of the Red River, but data do not support definitive conclusions.

Sampling Designs to Monitor Future Water-Quality Trends

The time-series model used to detect concentration trends for this report also was used to evaluate sampling designs to monitor future water-quality trends. As indicated in the previous section, the interpretation of trends in terms of cause and effect can be difficult and, although the data definitely indicate that trends are occurring, establishing a cause for the trends may require more extensive data gathering and model development. However, to evaluate the various sampling designs for this report, no interpretation of cause and effect was needed because the designs depended only on the statistical properties of the high-frequency variability in concentration (eq. 1), and the statistical properties of the high-frequency variability were independent of the trends (appendix 1).

To evaluate sampling designs, the number of samples collected (on average) each year needs to be considered along with the sampling dates and whether the number of samples or sampling dates should be variable or fixed (the same year after year). To determine whether the number of samples or the sampling dates should be variable or fixed, an objective of the trend analysis needs to be specified. Without specific trend-analysis objectives and assuming that trends can occur at any time, in any direction, and for any duration, a reasonable approach for trend monitoring is to collect a fixed number of samples each year. The sampling dates also should remain relatively fixed to reduce the variability of the noise. However, sampling on the exact same days each year is neither feasible nor necessary.

Given that the number of samples and the sampling dates remain fixed, two related concepts (sensitivity and efficiency) were used to evaluate sampling designs. Sensitivity measures the ability of a design to detect a trend—the smaller the trend that can be detected, the more sensitive the design. An efficient design maximizes the sensitivity to detect a trend for a fixed cost, which for this report was measured in terms of the number of samples per year. The only way to increase the sensitivity of an efficient design is to increase the cost—that is, to collect samples more frequently. For example, among all possible twosample designs, the most efficient design might be to sample once during April and once during August, and among all possible three-sample designs, the most efficient design might be to sample once in April, once in August, and once in December. The best three-sample design is more sensitive than the best two-sample design but also is more costly. Therefore, to determine whether three samples are preferable to two samples, judgment is needed as to whether the increased sensitivity is worth the increased cost.

For the design analysis in this report, the assumptions were made that a streamflow gage would continue to be operated at each station (so that the future streamflow-related variability could be removed) and that concentration data would be collected no more than once each month. Concentration data potentially could be collected more often, but the cost of such data collection would be prohibitive. The assumption also was made that the concentration data would be collected near the fifth day of the month. However, the actual sampling date could vary from 1 week before to 1 week after the fifth day without appreciably changing the results of the design analysis.

The sensitivity of a sampling design depends on the duration of the trend. If concentrations are increasing at a rate of 5 percent per year, the chance of detecting the trend after only 1 year may be extremely small. However, if the trend persists for 5 years, the chance of detecting the trend increases dramatically. In contrast to the sensitivity of a design, the efficiency of a design is not dependent on the duration of the trend. If a particular four-sample (per year) design is most efficient for detecting a trend that persists for 5 years, that design generally will be most efficient for detecting a trend that persists for 2 years or 10 years. Therefore, a 5-year duration was used as a benchmark to determine which designs in the design analysis were most efficient.

Even if a trend persists for 5 years or longer, sampling designs cannot detect trends with absolute certainty or prove that no trends exist with absolute certainty. Therefore, the size of the trend that can be detected depends on the acceptable level of tolerance for incorrectly identifying a trend. For this report, the acceptable level of tolerance was controlled by specifying two probabilities—the probability that a true trend was detected and the probability that a trend was detected when no true trend existed. Because the selection of an efficient design is not highly dependent on the values specified for the two probabilities, for this report, the first probability was set equal to 0.5 and the second probability (also called the type-I error probability) was set equal to 0.1. The designs then were compared in terms of their characteristic trends. The characteristic trend of a design, which is computed as described by Vecchia (2003b), is the increase or decrease in concentration during a 5-year period, in percent, that has a 50-percent chance of being detected using a type-I error probability of 0.1. Trends larger than the characteristic trend have more than a 50-percent chance of being detected, and trends smaller than the characteristic trend have less than a 50-percent chance of being detected. The characteristic trend is used in this report as a benchmark to compare the sensitivity of the various sampling designs.

Sampling designs first were evaluated with regard to their sensitivity to detect annual trends, which are trends that occur uniformly throughout the year. Then, the designs were evaluated with regard to their sensitivity to detect trends that occurred during three 4-month seasons—March through June, July through October, and November through February. Additional samples were added to the annual design, if warranted, to increase the sensitivity to detect trends for certain constituents and seasons.

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An efficient design for one constituent may be an inefficient design for another constituent. Therefore, designs needed to be evaluated with regard to their overall ability to detect trends in the whole suite of constituents. The design results for the smaller tributary stations were not included in this report because the designs for those stations could not be evaluated for nutrients and dissolved trace metals because of too few data. The design results for major ions and dissolved solids for the small tributary stations were similar to those for the main-stem and major tributary stations.

Detection of Annual Trends

An annual trend is a trend that occurs uniformly throughout the year. Thus, for example, an annual trend in total phosphorus concentration of 50 percent during 5 years means that the median total phosphorus concentration in every month increased by 50 percent from the beginning to the end of the 5-year interval. A total of 4,095 potential sampling designs with, at most, one sample per month were analyzed for the detection of annual trends for this report. However, detailed analysis of the sensitivity of the designs indicated that a small subset of the designs could be used to demonstrate the general design princi-

ples that emerged. Therefore, only a small subset of the potential designs considered is shown in this report.

The characteristic annual trends for dissolved sulfate concentrations for the main-stem and major tributary stations are shown in figure 23. As indicated by the solid boxes in the figure, designs 1 though 6 consist of a single sample per year. Design 4, with a single sample in April, has a characteristic trend of about 160 percent for the Red River at Hickson, N. Dak., station (site 1). Therefore, dissolved sulfate concentrations for that station would need to increase by about 160 percent during a 5-year interval for a 50-percent chance of detecting the trend. In contrast, design 4 has a characteristic trend of 55 percent for the Sheyenne River near Kindred, N. Dak., station (site 3). Designs 1 through 6 indicate that, with the exception of the Kindred station (site 3), the characteristic trend is highly dependent on when the sample is collected. For example, for the Red River at Emerson, Manitoba, station (site 9), design 5, with a single sample in June, has a characteristic trend of about 40 percent. However, design 3, with a single sample in February, has a characteristic trend of more than 200 percent. Design 3 is an efficient one-sample design for the Hickson station (site 1), the Kindred station (site 3), the Red River at Halstad, Minn., station (site 4), and the Red Lake River at Crookston, Minn., station (site 6) but a highly inefficient

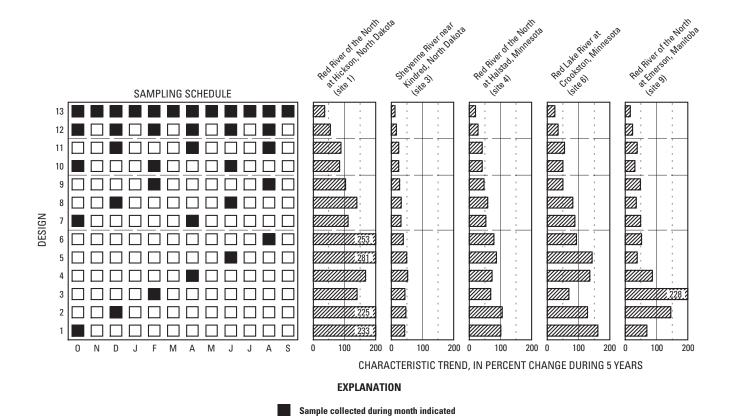


Figure 23. Characteristic annual trends for selected sampling designs for dissolved sulfate concentrations for main-stem and major tributary stations.

design for the Emerson station (site 9). In contrast, design 5 is an efficient one-sample design for the Emerson station (site 9) but a highly inefficient design for the Hickson station (site 1).

Designs 7 through 13 (fig. 23) are balanced designs that consist of 2, 3, 6, or 12 samples per year. Balanced designs, in which samples are spaced uniformly throughout the year, tend to be more efficient for the detection of annual trends in multiple constituents than unbalanced designs, in which samples are concentrated during certain times of year. The characteristic trends in sampling designs generally decrease as the number of samples increases, and less variability occurs between designs as the number of samples increases. However, the incremental improvements in sensitivity diminish rapidly as the number of samples increases to more than three per year. For example, the characteristic trends decreased more from design 11, with 3 samples per year, to design 12, with 6 samples per year, than from design 12 to design 13, with 12 samples per year. To select the most efficient designs to monitor water-quality trends, goals can be set for sensitivity. The most efficient designs for meeting those goals then are selected to monitor the water-quality trends. For example, if the goal is to have a reasonable chance of detecting a trend in sulfate concentration of 50 percent or more for every station, the characteristic trends should all be less than 50 percent. This goal can be achieved with design 13, with 12 samples per year, for the Hickson station (site 1); design 6, with 1 sample in August, for the Kindred station (site 3); design 11, with 3 samples per year, for the Halstad station (site 4); design 12, with 6 samples per year, for the Crookston station (site 6); and design 5, with 1 sample in June, for the Emerson station (site 9). These results indicate that, if the most efficient designs are selected to monitor water-quality trends, the number and timing of samples may differ substantially from station to station. However, in a water-quality monitoring program, these differences might be impractical. For example, design 13 for the Hickson station (site 1) may not be justified because of the high cost of the design. Therefore, a less expensive design may be preferable for that station although the sensitivity goal would not be met. Conversely, design 6 for the Kindred station (site 3) and design 5 for the Emerson station (site 9) might meet the sensitivity goal with little cost but would not allow the verification of a uniform annual trend because no samples are collected during most of the year. Logistical reasons also may exist for maintaining balance between stations. For example, the Hickson station (site 1), the Kindred station (site 3), and the Halstad station (site 4) are in close proximity to one another and could be sampled in one trip. Thus, less expense probably would be incurred to maintain design 12 for all three stations than to maintain design 13 for a single station.

The characteristic annual trends for total ammonia plus organic nitrogen concentrations (fig. 24) confirm many of the observations discussed for dissolved sulfate. Namely, the characteristic trends for designs 1 through 6, with a single sample per year, are dependent on when the sample is collected, and the most efficient time to collect a single sample differs among sta-

tions. For example, design 5, with a single sample in June, has a characteristic trend of about 70 percent for the Crookston station (site 6) and is the most efficient one-sample design for that station. However, the same design has a characteristic trend of about 150 percent for the Emerson station (site 9) and is the least efficient design for that station. The characteristic trends decrease substantially when the number of samples increases from one to three per year, but the incremental decreases are small when the number increases to more than three per year. Design 11, with three samples per year, has good sensitivity for detecting annual trends for all stations. The characteristic trends for that design are all less than 50 percent.

The most efficient one-sample design for dissolved sulfate for a particular station may be a highly inefficient one-sample design for total ammonia plus organic nitrogen. For example, for dissolved sulfate (fig. 23), design 5, with a single sample in June, has a characteristic trend of about 40 percent for the Emerson station (site 9) and is the most efficient one-sample design for that station. However, for total ammonia plus organic nitrogen (fig. 24), the same design has a characteristic trend of about 150 percent for the Emerson station (site 9) and is the least efficient one-sample design for that station. For dissolved sulfate for the Crookston station (site 6), design 5 has a characteristic trend of about 150 percent and is the least efficient one-sample design. However, for total ammonia plus organic nitrogen for the Crookston station (site 6), design 5 has a characteristic trend of about 70 percent and is the most efficient one-sample design.

The characteristic annual trends for the remaining constituents (not shown) also confirm many of the observations discussed previously. The most efficient one-sample design differed from station to station and constituent to constituent. However, balanced designs, with three to six samples per year, tended to be efficient designs that had reasonable sensitivity for detecting trends for most stations and constituents. Designs with fewer than three samples per year and/or designs that targeted certain times of the year generally had low sensitivity for detecting annual trends for certain constituents. Among the balanced designs with three to six samples per year, the sensitivity for detecting annual trends was not particularly dependent on when the samples were collected as long as relatively uniform spacing existed between the samples. Increasing the number of samples to more than six per year generally resulted in small incremental improvements in sensitivity for detecting annual trends. However, the improvement in sensitivity may not justify the cost of the additional samples.

Detection of Seasonal Trends

Sampling designs that are sensitive for detecting annual trends may not be sensitive for detecting seasonal trends. However, from a trend-monitoring perspective, trends that occur in certain constituents only during certain times of the year may be important. For example, most of the snowmelt and rainfall run-

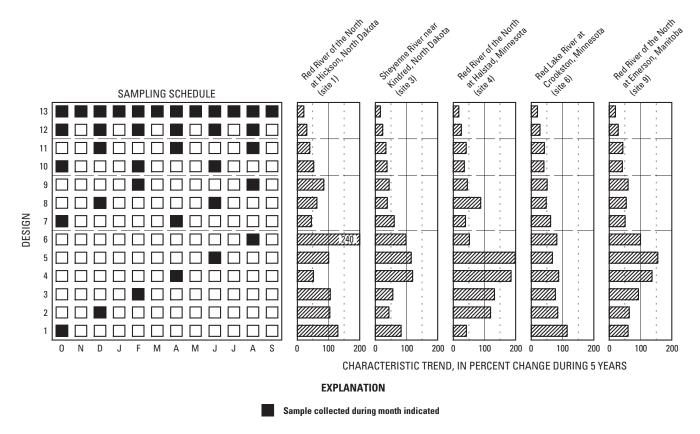


Figure 24. Characteristic annual trends for selected sampling designs for total ammonia plus organic nitrogen concentrations for main-stem and major tributary stations.

off in the Red River Basin occurs from March through June. Therefore, the spring and early summer runoff season probably is most important for monitoring trends in constituents, such as dissolved sulfate and total ammonia plus organic nitrogen, that have sources that extend throughout large parts of the basin and from which most of the constituent is transported to the stream in surface runoff. Other constituents, such as dissolved chloride and dissolved nitrite plus nitrate as nitrogen, may have substantial ground-water sources. Thus, monitoring trends for those constituents during low-flow conditions may be most important. Still other constituents, such as total phosphorus and dissolved iron, may have a complex combination of point sources, ground-water sources, and nonpoint sources and may require monitoring during all flow conditions. Likewise, constituents that are known to be affected by agricultural tillage or fertilizer application may require more extensive monitoring during the growing season, constituents known to be affected by urban or industrial wastewater discharge may require more extensive monitoring during the fall and winter, and constituents known to be affected by livestock production may require more extensive monitoring during early spring.

To ensure that the sampling designs in this report maintained a reasonable balance for detecting seasonal trends for all

constituents and seasons, the designs were evaluated with respect to their sensitivity for detecting trends that occurred during three 4-month seasons—March through June, which typically includes the spring breakup and high-flow season; July through October, which typically includes the summer and fall low-flow season; and November through February, which typically includes the late fall and winter freezeup. Seasonal trends were assumed to begin during any month of the selected season and to persist for 4 months. For example, for season 1 (March through June), a trend could begin in March and end in June, begin in April and end in July, begin in May and end in August, or begin in June and end in September. Thus, some overlap may have occurred between seasons—for example, a trend that occurred from June through September (season 1) would overlap with a trend that occurred from July through October (season 2). The overlap between seasons ensured a gradual transition of the characteristic trends from one season to the next. The characteristic trend for a particular season is the average of the characteristic trends for each of the four potential starting months in that season. Thus, for example, a characteristic trend of 75 percent for season 1 means that, on average, concentrations in any 4-month period beginning in season 1 would need to increase 75 percent during a 5-year period to have a 50-percent chance of being detected. Although the characteristic trend may differ somewhat depending on the starting month, the average trend is a reasonable measure of the overall sensitivity for the season.

The evaluation of sampling designs for detecting seasonal trends began with selecting a "baseline" design for detecting annual trends. The baseline design consisted of three samples spaced 4 months apart so that every possible 4-month window had at least one sample. Annual designs 10 and 11 (fig. 24) were two possible baseline designs. The conclusions of the design analysis for detecting seasonal trends were not affected by the choice of the baseline design; therefore, the annual design, with samples in December, April, and August, was used for the analysis. Samples were selectively added to that design to achieve a balance of sensitivity for detecting trends in the various seasons. Additional samples were targeted for specific constituents or seasons to achieve the most gain in information from each additional sample.

The characteristic seasonal trends for dissolved sulfate concentrations for the main-stem and major tributary stations are shown in figure 25. Designs 1 through 5 indicate the sensitivity for detecting trends that occurred in season 1 (March through June). For designs 1 through 5, samples were selectively added to the baseline design in May, June, or July. For discussion purposes, a design will be said to have good sensitivity for detecting trends if the characteristic trend of the design is less than 50 percent, moderate sensitivity if the trend is between 50 and 100 percent, and poor sensitivity if the trend is greater than 100 percent. Design 1 had poor sensitivity for detecting a trend in dissolved sulfate concentration in season 1 for the Red River at Hickson, N. Dak., station (site 1) and the Red Lake River at Crookston, Minn., station (site 6), moderate sensitivity for the Red River at Halstad, Minn., station (site 4) and the Red River at Emerson, Manitoba, station (site 9), and good sensitivity for the Sheyenne River near Kindred, N. Dak., station (site 3). Design 2, with an additional sample in June, had considerably better sensitivity than design 1 for all stations except the Kindred station (site 3) and is a good alternative to design 1. Design 2 also had moderate or good sensitivity for all stations except the Hickson station (site 1). For that station, an additional sample in May, July, or both, might be considered if dissolved sulfate is of prime importance. Designs 6 through 10 indicate the sensitivity for detecting trends that occurred in season 2 (July through October). The characteristic trends for those designs are similar to the trends for designs 1 through 5 for season 1. Design 7, with an additional sample in October, had moderate to good sensitivity for all stations except the Hickson station (site 1) and is a good alternative to design 6 for most stations. An additional sample in September, November, or both, might be considered to improve sensitivity for the Hickson station (site 1). Designs 11 through 15 indicate the sensitivity for detecting trends that occurred in season 3 (November through February). Design 12 has moderate or good sensitivity for all stations and is a good alternative to design 11.

The characteristic seasonal trends for dissolved chloride concentrations (not shown) were similar to those for dissolved sulfate. For the Hickson station (site 1), the Crookston station (site 6), and the Emerson station (site 9), the baseline design had poor sensitivity for detecting trends for all three seasons. However, bimonthly sampling (the combination of designs 2, 7, and 12) resulted in moderate to good sensitivity for all three stations and all three seasons. For the Kindred station (site 3) and the Halstad station (site 4), the baseline design had moderate sensitivity for all three seasons, and bimonthly sampling resulted in good sensitivity for all three seasons.

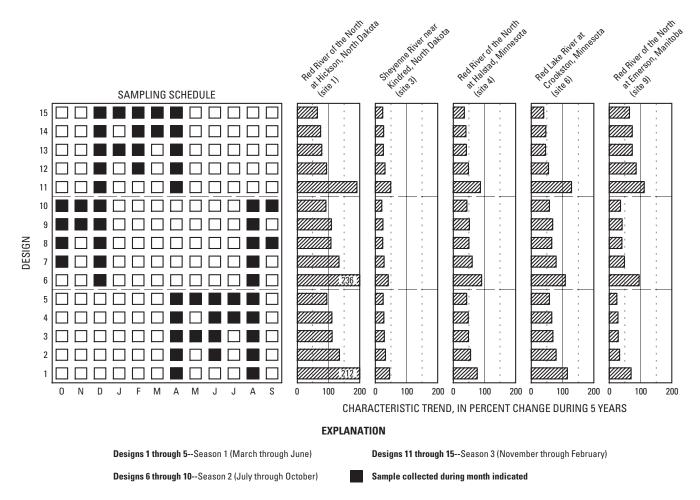
The characteristic seasonal trends for dissolved-solids concentrations (not shown) indicate the baseline design had good sensitivity for all five stations and all three seasons. The trends for dissolved solids generally were much smaller than the trends for dissolved sulfate and dissolved chloride. Because dissolved solids consist of the sum of the individual dissolved constituents, including sulfate and chloride, much of the high-frequency variability in the individual constituents is smoothed, making trends easier to detect. However, monitoring trends for individual ions, such as sulfate and chloride, may be more important than monitoring trends for dissolved solids and also may provide more insight into the potential causes of the trends.

The characteristic seasonal trends for dissolved nitrite plus nitrate as nitrogen concentrations (fig. 26) were larger for the main-stem stations than for the tributary stations. However, because the tributary stations had a high percentage of censored values, the trends for those stations may not be accurate. The trends for the main-stem stations were large for both seasons 1 and 3. To achieve characteristic trends of less than 150 percent for the main-stem stations, seven samples (the combination of designs 5, 6, and 12) would suffice.

The characteristic seasonal trends for total ammonia plus organic nitrogen concentrations (fig. 27) were similar for all stations. The baseline design had poor sensitivity for detecting trends for one or more stations in each of the three seasons. Bimonthly sampling (the combination of designs 2, 7, and 12) resulted in substantial improvements in sensitivity, especially for the Hickson station (site 1) and the Halstad station (site 4) and also resulted in moderate or good sensitivity for all five stations and all three seasons.

The characteristic seasonal trends for total phosphorus concentrations (fig. 28) generally were larger than those for total ammonia plus organic nitrogen (fig. 27). The total phosphorus concentrations also tended to have more high-frequency variability than the total ammonia plus organic nitrogen concentrations [as indicated by a higher standard deviation of HFV_C (eq. 1)]. Thus, the trends for total phosphorus were more difficult to detect than those for total ammonia plus organic nitrogen. The baseline design had poor sensitivity for most stations and seasons, and, in many cases, had a characteristic trend of more than 200 percent. Bimonthly sampling (the





Characteristic seasonal trends for selected sampling designs for dissolved sulfate concentrations for main-stem and major tributary stations.

combination of designs 2, 7, and 12) resulted in substantial improvements in sensitivity for most stations and seasons, but, in many cases, still resulted in poor sensitivity. The combination of designs 2, 9, and 13 for a total of eight samples (monthly sampling from October to February and bimonthly sampling from April to August) resulted in moderate or good sensitivity for the Hickson station (site 1), the Kindred station (site 3), and the Halstad station (site 4). However, to achieve moderate sensitivity for the remaining stations, monthly sampling would be required. If monthly sampling is not feasible, a more reasonable goal for total phosphorus might be to achieve characteristic trends of less than 150 percent. That goal could be achieved for all five stations with a total of seven samples (the combination of designs 3, 7, and 12).

Considering the previous discussion for dissolved nitrite plus nitrate as nitrogen and total phosphorus, the combination of designs 5, 7, and 12 would achieve characteristic trends of less than 150 percent for both dissolved nitrite plus nitrate as nitrogen and total phosphorus. Thus, eight samples per year

(monthly sampling from April to August and bimonthly sampling from October to February) might be a reasonable design for detecting trends in both dissolved nitrite plus nitrate as nitrogen and total phosphorus.

The characteristic seasonal trends for dissolved iron and dissolved manganese (not shown) were qualitatively similar to those for dissolved nitrite plus nitrate as nitrogen and total phosphorus. However, the trends for the dissolved trace metals were higher than those for the nutrients. The combination of designs 5, 7, and 12 resulted in characteristic trends of less than 200 percent for the dissolved trace metals. However, the large percentage of censored values for the trace metals may have caused inaccuracies in the computed trends.

The previous discussions for detecting trends in dissolvedion, nutrient, and dissolved trace-metal concentrations for the Red River Basin indicate a reasonable overall design for detecting trends for all stations and constituents consisted of eight samples per year, with monthly sampling from April through

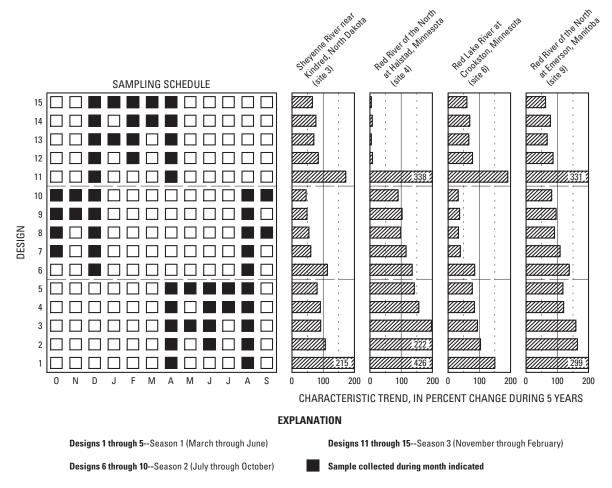


Figure 26. Characteristic seasonal trends for selected sampling designs for dissolved nitrite plus nitrate as nitrogen concentrations for main-stem and major tributary stations.

August and bimonthly sampling from October through February. For major dissolved ions, dissolved solids, and total ammonia plus organic nitrogen, the characteristic seasonal trends for that design generally were less than 100 percent and often were less than 50 percent. For dissolved nitrite plus nitrate as nitrogen and total phosphorus, the characteristic seasonal trends for that design generally were less than 150 percent and often were less than 100 percent. For dissolved trace metals, the characteristic seasonal trends for that design generally were less than 200 percent. Fewer samples may result in considerable loss of sensitivity for detecting trends for one or more constituents during one or more of the 4-month seasons. Additional samples may be required to meet specific objectives or to improve sensitivity for some constituents, but the additional samples generally resulted in small incremental improvements in sensitivity and may not justify the additional cost.

Summary

The Red River of the North (Red River) Basin at Emerson, Manitoba, encompasses about 35,000 square miles of rich agricultural lands, forests, wetlands, and prairies and contains numerous lakes and prairie potholes. The Bureau of Reclamation is considering several alternatives to meet the future municipal, rural, and industrial water-supply needs in the basin, and an environmental impact statement is being prepared to evaluate the potential effects of the various alternatives on the water quality and aquatic health in the basin in relation to the historical variability in streamflow and constituent concentration. Therefore, a water-quality trend analysis was needed to determine the amount of natural water-quality variability that can be expected to occur in the basin, to determine if significant waterquality changes have occurred as a result of human activities, to explore potential causal mechanisms for water-quality changes, and to establish a baseline from which to monitor future waterquality trends. This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the

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EXPLANATION

Designs 1 through 5--Season 1 (March through June)

Designs 1 through 15--Season 3 (November through February)

Designs 6 through 10--Season 2 (July through October)

Sample collected during month indicated

200

Figure 27. Characteristic seasonal trends for selected sampling designs for total ammonia plus organic nitrogen concentrations for main-stem and major tributary stations.

Bureau of Reclamation, to analyze historical water-quality trends in dissolved major ions (sulfate and chloride), dissolved solids, nutrients (dissolved nitrite plus nitrate as nitrogen, total ammonia plus organic nitrogen, and total phosphorus), and dissolved trace metals (iron and manganese) for nine streamflow-gaging stations in the basin.

Annual variability in streamflow in the Red River Basin was high during the trend-analysis period (1970-2001). The annual variability affects constituent concentrations in individual tributaries to the Red River and, in turn, affects constituent concentrations in the main stem of the Red River because of the relative streamflow contribution from the tributaries to the main stem. Therefore, an annual concentration anomaly, which is an estimate of the interannual variability in concentration that can be attributed to long-term variability in streamflow, was used to analyze annual streamflow-related variability in constituent concentrations. The effect of the streamflow-related variability on concentrations differed depending on the hydrologic properties of the basins and the relative importance of the different

sources (ground-water, surface-runoff, or point sources) of chemical constituents. During 1992, at the end of a severe drought, the median dissolved sulfate concentrations for the largest North Dakota tributary (the Sheyenne River) were lower than at any other time during 1970-2001 because dissolved sulfate concentrations in the ground-water discharge were lower than in the surface runoff. However, the median dissolved sulfate concentrations for the largest Minnesota tributary (the Red Lake River) were higher in 1992 than at any other time during 1970-2001 because dissolved sulfate concentrations in the ground-water discharge were higher than in the surface runoff. Median dissolved sulfate concentrations for the main-stem stations (the Red River at Hickson, N. Dak., the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations) were low during 1992 because Minnesota tributaries, which had lower dissolved sulfate concentrations than North Dakota tributaries, contributed a higher percentage of streamflow to the main stem during the drought. In contrast to the dissolved sulfate concentrations, median total phosphorus concentrations for the same main-stem stations during 1988-92 were higher than

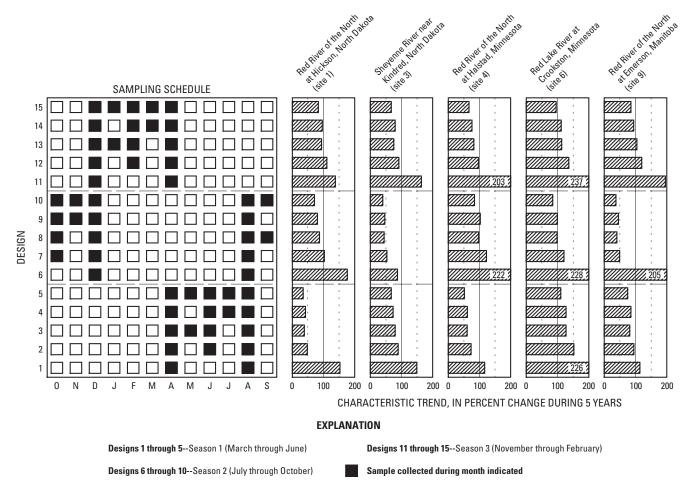


Figure 28. Characteristic seasonal trends for selected sampling designs for total phosphorus concentrations for main-stem and major tributary stations.

concentrations during normal or wet years as a result of high total phosphorus concentrations for ungaged tributaries during that time or as a result of contributions from point sources of phosphorus along the main stem. During 1995-2000 (the wettest 5-year period analyzed), median total phosphorus concentrations for the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations were lower than at any other time during 1970-2001 because of generally low total phosphorus concentrations for tributary flows and dilution of contributions from point sources of total phosphorus.

The concentration trend is an estimate of the long-term systematic changes in concentration that are unrelated to seasonal or long-term variability in streamflow. The time-series model for this report was used to remove natural seasonal and annual variability to make the concentration trends easier to detect. Concentrations that have both the seasonal and annual variability removed are called standardized concentrations. Numerous changes that could not be attributed to natural streamflow-related variability occurred in the standardized con-

centrations during the trend-analysis period. During various times from the late 1970's to the mid-1990's, significant increases in standardized dissolved sulfate, dissolved chloride, and dissolved-solids concentrations occurred for eight of the nine stations analyzed. Although significant decreases also occurred for some stations during various times from the mid-1970's to the early 1980's, standardized dissolved chloride and dissolved sulfate concentrations generally were higher at the end of the trend-analysis period than at any other time.

The fitted trends for standardized dissolved nitrite plus nitrate as nitrogen concentrations indicated highly significant increases in the median standardized concentrations occurred from the mid-1980's to the mid-1990's for the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations. The median standardized concentrations for the tributary stations either decreased or remained nearly stable from the early 1980's to the mid-1990's. The increasing concentrations for the main-stem stations indicate the upward trends may have been

caused by human activities along the main stem of the Red River.

Significant trends for standardized total ammonia plus organic nitrogen concentrations occurred for all stations except the Red River at Crookston, Minn., station. Median standardized concentrations for the Sheyenne River near Kindred, N. Dak., Red River at Halstad, Minn., and Red River at Emerson, Manitoba, stations increased from the late 1970's to the early 1980's and then decreased from the early 1980's to the mid-1990's. A highly significant decrease in the median standardized concentrations occurred from the early 1980's to the mid-1990's for the Red River at Hickson, N. Dak., station. For all stations except the Crookston station, the lowest median standardized concentrations occurred at the end of the trendanalysis period.

The fitted trends for standardized total phosphorus concentrations for the Sheyenne River near Kindred, N. Dak., station increased from the late 1970's to the early 1980's and decreased from the early 1980's to the mid-1990's. The fitted tends for the Red Lake River at Crookston, Minn., station also decreased from the early 1980's to the mid-1990's. The lowest median standardized concentrations for both stations occurred at the end of the trend-analysis period. Small but insignificant increases occurred for the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations.

No trends were detected for standardized dissolved iron or dissolved manganese concentrations. However, the combination of extreme high-frequency variability, few data, and the number of censored values may have disguised the streamflowrelated variability for iron.

A full analysis of cause and effect would require a dynamic source-and-transport watershed model and was beyond the scope of this study. However, the fitted trends for the nutrient concentrations were compared to known changes in human activities during 1970-2001 to identify which changes were related to the fitted trends and which changes probably were not related to the fitted trends. The fitted trends for total ammonia plus organic nitrogen concentrations were consistent with cropland changes that occurred during 1970-2001. The increasing concentrations for the Sheyenne River near Kindred, N. Dak., Red River at Halstad, Minn., and Red River at Emerson, Manitoba, stations from the late 1970's to the early 1980's, followed by decreasing concentrations from the early 1980's to the mid-1980's, were consistent with the large increases, followed by large decreases, of total cropland (mostly sunflowers) that occurred in western parts of the basin during those periods. Decreases in total ammonia plus organic nitrogen concentrations for those stations from the mid-1980's to the mid-1990's coincided with a large change of cropland from wheat to soybeans (which presumably resulted in a decrease in application of nitrogen fertilizer) during that time. Although livestock inventories generally decreased during 1970-2001, either the

decrease had little effect on organic nitrogen concentrations or the effect was offset.

The increases in dissolved nitrite plus nitrate as nitrogen concentrations for the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations probably were not caused by changes in cropland or livestock-related activities. Although a definitive cause for the increases cannot be determined without additional data, the increases may have been related to municipal wastewater discharges, urban runoff, or industrial sources in the Fargo, N. Dak.-Moorhead, Minn., area.

The downward trends in total phosphorus concentrations for the Red Lake River at Crookston, Minn., station may be related to changes in livestock-related activities. Although no significant trends were detected for the main-stem stations, small but insignificant increases were detected for the Red River at Halstad, Minn., and the Red River at Emerson, Manitoba, stations. Changes in cropland or livestock-related activities probably would cause a decrease in total phosphorus concentrations. Phosphorus concentrations may have increased from urban runoff or industrial sources in the Fargo-Moorhead area or from other sources along the main stem of the Red River.

The time-series model used to detect historical concentration trends also was used to evaluate sampling designs to monitor future water-quality trends. Various sampling designs were evaluated with regard to their sensitivity to detect both annual and seasonal trends during three 4-month seasons. Sensitivity of the designs was evaluated by comparing the characteristic trends of the designs, defined as the size of trend that had a reasonable chance (greater than 50 percent) of being detected after 5 years of sampling. The smaller the characteristic trend, the more sensitive the design. A reasonable overall design for detecting trends for all stations and constituents consisted of eight samples per year, with monthly sampling from April through August and bimonthly sampling from October through February. For dissolved major ions, dissolved solids, and total ammonia plus organic nitrogen, the characteristic trends for that design generally were less than 100 percent and often were less than 50 percent for each 4-month season. For dissolved nitrite plus nitrate as nitrogen and total phosphorus, the characteristic trends for that design generally were less than 150 percent and often were less than 100 percent. For dissolved trace metals, the characteristic trends for that design generally were less than 200 percent.

References

Booy, C., and Lye, L.M., 1986, Accumulated basin storage as a factor in the correlation structure of annual peak flows on the Red River: Canadian Journal of Civil Engineering, v. 13, p. 365-74.

- Hem, J.D., 1992, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- Hirsch, R.M., Slack, J.R., and Smith, R.A., 1982, Techniques of trend analysis for monthly water quality data: Water Resources Research, v. 18, no. 1, p. 107-121.
- Jones, G., and Armstrong, N., 2001, Long-term trends in total nitrogen and total phosphorus concentrations in Manitoba streams: Water Quality Management Section, Water Branch, Manitoba Conservation, Report No. 2001-07, 154 p.
- Litke, D.W., 1999, Review of phosphorus control measures in the United States and their effects on water quality: U.S. Geological Survey Water-Resources Investigations Report 99-4007, 38 p.
- Macek-Rowland, K.M., and Dressler, V.M., 2002, Statistical summaries of water-quality data for selected streamflow-gaging stations in the Red River of the North Basin, North Dakota, Minnesota, and South Dakota: U.S. Geological Survey Open-File Report 02-390, 229 p.
- Salas, J.D., Tabois, G.Q., and Bartolini, P., 1985, Approaches to multivariate modeling of water resources time series: Water Resources Bulletin, v. 21, no. 4, p. 683-708.
- Sether, B.A., Berkas, W.R., and Vecchia, A.V., 2004, Constituent loads and flow-weighted average concentrations for major subbasins of the upper Red River of the North Basin, 1997-99: U.S. Geological Survey Scientific Investigations Report 2004-5200, 62 p.
- Smith, R.A., and Alexander, R.B., 2000, Sources of nutrients in the Nation's watersheds: Proceedings of the Natural Resource, Agriculture, and Engineering Service Conference for Nutrient Management Consultants, Extension Educators, and Producer Advisors, March 28-30, 2000, Camp Hill, Pennsylvania, 8 p.
- Stoner, J.D., Lorenz, D.L., Wiche, G.J., and Goldstein, R.M., 1993, Red River of the North Basin, Minnesota, North Dakota, and South Dakota: Water Resources Bulletin, v. 29, no. 4, p. 575-615.
- Strobel, M.L., and Haffield, N.D., 1995, Salinity in surface water in the Red River of the North Basin, northeastern North Dakota: U.S. Geological Survey Water-Resources Investigations Report 95-4082, 14 p.

- Tornes, L.H., and Brigham, M.E., 1994, Nutrients, suspended sediment, and pesticides in waters of the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1970-90: U.S. Geological Survey Water-Resources Investigations Report 93-4231, 62 p.
- Trench, E.C., and Vecchia, A.V., 2002, Water-quality trend analysis and sampling design for streams in Connecticut, 1968-98: U.S. Geological Survey Water-Resources Investigations Report 02-4011, 94 p.
- U.S. Department of Agriculture, National Agricultural Statistics Service: accessed June 25, 2002, at http://www.nass.usda.gov
- U.S. Department of the Interior, Bureau of Reclamation, 2005, Reclamation, Managing water in the west--Executive summary, Draft report on Red River Valley water needs and options: 24 p.
- Vecchia, A.V., 1985, Periodic autoregressive moving average (PARMA) modeling with applications to water resources: Water Resources Bulletin, v. 21, p. 721-730.
- Vecchia, A.V., 2000, Water-quality trend analysis and sampling design for the Souris River, Saskatchewan, North Dakota, and Manitoba: U.S. Geological Survey Water-Resources Investigations Report 00-4019, 77 p.
- Vecchia, A.V., 2003a, Relation between climate variability and stream water quality in the continental United States: Hydrological Science and Technology, v. 19, no. 1, p. 77-98.
- Vecchia, A.V., 2003b, Water-quality trend analysis and sampling design for streams in North Dakota, 1971-2000: U.S. Geological Survey Water-Resources Investigations Report 03-4094, 73 p.
- Wiche, G.J., Vecchia, A.V., Osborne, L., Wood, C.M., and Fay, J.T., 2000, Climatology, hydrology, and simulation of an emergency outlet, Devils Lake Basin, North Dakota: U.S. Geological Survey Water-Resources Investigations Report 00-4174, 16 p.
- Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., eds., 1998, National field manual for the collection of water quality: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1-A9, variously paginated.

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Appendix 1. Time-Series Model for Streamflow and Concentration

The time-series model used in this report to analyze waterquality trends is a modified version of the model first introduced by Vecchia (2000). The streamflow data were expressed as

$$\log(Q) = M_O + ANN_O + SEAS_O + HFV_O \tag{1-1}$$

where

log denotes the base-10 logarithm;

Q is streamflow, in cubic feet per second;

 M_Q is the long-term mean of the logtransformed streamflow, as the base-10 logarithm of cubic feet per second;

 ANN_Q is the annual streamflow anomaly (dimensionless);

 $SEAS_Q$ is the seasonal streamflow anomaly (dimensionless); and

 HFV_Q is the high-frequency variability of the streamflow (dimensionless).

The concentration data were expressed as

$$\begin{split} \log(C) &= M_C + ANN_C + SEAS_C \\ &+ TREND_C + HFV_C \end{split} \tag{1--2}$$

where

log denotes the base-10 logarithm;

C is the concentration, in milligrams or micrograms per liter;

 M_C is the long-term mean of the logtransformed concentration, as the base-10 logarithm of milligrams or micrograms per liter;

 ANN_C is the annual concentration anomaly (dimensionless);

 $SEAS_C$ is the seasonal concentration anomaly (dimensionless);

 $TREND_C$ is the concentration trend (dimensionless); and

 HFV_C is the high-frequency variability of the concentration (dimensionless).

Although the trend-analysis period for the concentration data was 1970-2001, temporally lagged streamflows for lags of as many as 5 years were used in the model. Therefore, daily streamflows for 1965-2001 were used for the water-quality trend analysis. The long-term (logarithmic) mean for streamflow was estimated as the average of the log-transformed daily

streamflows for 1965-2001. The annual and seasonal streamflow anomalies were computed as described by Vecchia (2003a). The annual streamflow anomaly consists of a long-term and short-term anomaly and was expressed as

$$ANN_Q = LTANN_Q + STANN_Q \tag{1-3}$$

where

 $LTANN_Q$ is the long-term annual streamflow anomaly (dimensionless), and $STANN_Q$ is the short-term annual streamflow anomaly (dimensionless).

The long-term annual streamflow anomaly was computed for each time step, t (in decimal years), by averaging the deviations of log(Q) from the long-term mean for 5 years, up to and including time t, and is a measure of extended droughts and wet periods. The short-term annual streamflow anomaly was computed by averaging the deviations of log(Q) from the sum of the long-term mean and the long-term annual anomaly for 1 year, up to and including time t, and is a measure of shortterm annual variability in streamflow. The seasonal streamflow anomaly was computed by averaging the deviations of log(Q)from the sum of the long-term mean, the long-term annual anomaly, and the short-term annual anomaly for 3 months, up to and including time t, and is a measure of seasonal variability in streamflow. Finally, the high-frequency variability in streamflow was computed by subtracting the long-term mean, the long-term and short-term annual anomalies, and the seasonal anomaly from log(Q).

The components of equation 1–2 could not be computed directly from the concentration data because most concentration values were missing. Therefore, an equation that represented the annual and seasonal concentration anomalies was developed for the data used in this study. The resulting equation, which is similar to an equation that was developed in a national study (Vecchia, 2003a), is given by

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$$E[\log(C)|\log(Q)] = \alpha_0 \qquad (1-4)$$

$$+ \alpha_1 LTANN_Q$$

$$+ \alpha_2 STANN_Q$$

$$+ \alpha_3 (STANN_Q)^2$$

$$+ \alpha_4 SEAS_Q$$

$$+ \alpha_5 (SEAS_Q)^2$$

$$+ \alpha_6 \cos 2\pi t$$

$$+ \alpha_7 \sin 2\pi t$$

$$+ \alpha_8 \cos 4\pi t$$

$$+ \alpha_9 \sin 4\pi t$$

riates known to affect concentration (for example, fertilizer application, livestock production, impervious area, etc.) or can be constructed to fit a particular type of trend (step trend, linear trend, cyclic trend, etc.). In the water-quality trend analysis for this report, an exploratory approach was used to define the various functions, which were given by

$$f_{j}(t) = 0.5 + \frac{\left[\frac{t - m_{j}}{w_{j}}\right]}{1 + \frac{abs(t - m_{j})}{w_{j}}}, \text{ if } abs(t - m_{j}) < w_{j}; \quad (1-9)$$

$$f_i(t) = 0$$
, if $(t - m_i) < -w_i$; (1-10)

and

$$f_i(t) = 1$$
, if $(t - m_i) > w_i$ (1-11)

where

- is the midpoint for the jth trend func-
- is the half-width for the jth trend function.

various concentration anomalies were defined as

log(Q), and

 $\alpha_0, ..., \alpha_9$ are regression coefficients.

The coefficients (the α_i 's) in the equation were estimated as described later. In accordance with equations 1-2 and 1-4, the

 $E[\log(C)|\log(Q)]$ is the conditional

$$M_C = \alpha_0, \qquad (1-5)$$

expectation of log(C) given

$$ANN_C = \alpha_1 LTANN_Q + \alpha_2 STANN_Q$$

$$+ \alpha_3 (STANN_Q)^2,$$
(1-6)

and

where

$$SEAS_{C} = \alpha_{4}SEAS_{Q} + \alpha_{5}(SEAS_{Q})^{2} + \alpha_{6}\cos 2\pi t + \alpha_{7}\sin 2\pi t + \alpha_{8}\cos 4\pi t + \alpha_{9}\sin 4\pi t.$$

$$(1-7)$$

The concentration trend was represented as a linear combination of specified functions of time as follows:

$$TREND_C = \gamma_1 f_1(t) + \gamma_2 f_2(t) + \dots + \gamma_n f_n(t)$$
 (1–8)

where

$$\gamma_1, ..., \gamma_p$$
 are regression coefficients; $f_1(t), ..., f_p(t)$ are specified functions of t ; t is time, in decimal years; and p is the number of trend functions.

The coefficients in equation 1–8 were estimated as described later. The various functions of time, which can be specified to model virtually any type of trend, can be a time series of cova-

The functions given by equations 1–8 through 1-11 can be used to represent smooth, nonmonotonic trends in a manner similar to that used for polynomial splines. The midpoint and the half-width for the *j*th trend function and the number of trend functions were selected for each station and constituent as described later.

A bivariate, periodic autoregressive moving average (PARMA) model (Salas and others, 1985; Vecchia, 1985) was fitted to the high-frequency variability of streamflow and concentration to account for serial correlation and nonstationarity when estimating the coefficients in equations 1–5 through 1–8. The PARMA model used for this report was the same model described by Vecchia (2000), and the methodology for computing the Gaussian likelihood function (the likelihood function of the streamflow and concentration data assuming the high-frequency variability was normally distributed) is described in that report. Because computation of the likelihood function was complicated by the presence of missing concentration values, a Kalman filter algorithm, also described by Vecchia (2000), was used to recursively compute the likelihood function for the nonmissing values. The concentration anomalies, concentration trends, and PARMA model parameters were estimated jointly by maximizing the likelihood function or, equivalently, by minimizing minus twice the natural logarithm of the likelihood function as follows:

where

 $\alpha = [\alpha_0, \alpha_1, ..., \alpha_9]$ is a vector of parameters for the concentration anomalies (eqs. 1–5 through 1–7),

 $\gamma = [\gamma_1, \gamma_2, ..., \gamma_p]$ is a vector of parameters for the concentration trends (eq. 1–8),

 τ is a vector of parameters for the PARMA model (see Vecchia, 2000),

L is the Gaussian likelihood function,

X is the vector of log-transformed streamflows, and

Y is the vector of (nonmissing) logtransformed concentrations.

The parameter estimates obtained by minimizing equation 1–12 with respect to the parameters, α , γ , and τ , are called Gaussian maximum likelihood estimates. Gaussian maximum likelihood estimates have many desirable properties, such as being asymptotically (as the number of samples increases) unbiased, minimum-variance estimates even if the data are not normally distributed (subject to certain restrictions; see Vecchia, 2000). The significance level (or, equivalently, the P-value) for the concentration trend can be computed using the generalized likelihood ratio principle, which states that

$$GLR = \Lambda(\alpha^*, \gamma = 0, \tau^*) - \Lambda(\alpha^{\#}, \gamma^{\#}, \tau^{\#})$$
 (1-13)

where

GLR is the generalized likelihood ratio, $\alpha^* \text{ and } \tau^* \quad \text{are the maximum likelihood estimates} \\ \quad \text{of } \alpha \text{ and } \tau \text{ assuming } \gamma \text{ equals} \\ \quad \text{zero, and} \\ \alpha^\#, \gamma^\#, \text{ and } \tau^\# \quad \text{are maximum likelihood parameter} \\ \quad \text{estimates for the full model}$

is approximately chi-square distributed with degrees of freedom equal to p (the number of trend parameters). Generalized likelihood ratio tests also can be used to compute P-values (attained significance levels) for individual trend coefficients.

For this report, the number of trend functions and the midpoints and half-widths for the trend functions needed to be determined for each station and constituent. Therefore, a trend model was fitted to obtain the trend for the stations and constituents. To facilitate comparisons between the fitted trends for the different stations and constituents, the same initial model was fitted in each case and then simplified to obtain the fitted trend for each individual station and constituent. The initial model consisted of five trend functions (p = 5) with the following midpoints and half-widths: $m_1 = 1975$, $w_1 = 2.5$, $m_2 = 1980$, $w_2 = 2.5$, $m_3 = 1985$, $w_3 = 2.5$,

 m_4 = 1990, w_4 = 2.5, m_5 = 1995, and w_5 = 2.5. The midpoints thus were spaced 5 years apart and the duration (twice the half-width) of each trend was 5 years. The number of samples for the concentration data ultimately determines the complexity of the trend that can be detected. The closer the spacing between the midpoints, the more samples are required to estimate the fitted trend. Although trends of less than 5 years could have been included for some stations that had a high number of samples during certain periods, for most stations a 5-year duration was the smallest for which trends could reasonably be detected. For stations and constituents that had fewer than 10 samples before 1975 (table 4), the first trend function was not included in the initial model. Likewise, for stations that had fewer than 10 samples after 1995, the last trend function was not included.

The initial model was simplified for each station and constituent using the following procedure. First, trend functions were removed from the model one at a time, starting with the least significant, until all of the remaining trend coefficients were significant at the 20-percent level (the P-value of the generalized likelihood ratio test for the coefficient was less than 0.2). Then, the algebraic signs (plus or minus) of the remaining coefficients were used to combine adjacent trends. For example, if the fitted coefficients for the trend functions with $m_3 = 1985$ and $m_4 = 1990$ were both positive (or both negative), then the two trend functions were combined into a single function with m = 1987.5 and w = 5. Likewise, if the fitted coefficients for the trend functions with $m_3 = 1985$, $m_4 = 1990$, and $m_5 = 1995$ were all positive (or negative), all three functions were combined into a single function with m = 1990 and w = 7.5. After the trend functions were combined on the basis of the signs of the coefficients, the simplified model again was fitted using maximum likelihood and compared to the model with no trends (the model in which all of the trend coefficients were equal to zero). If the P-value of the trend was less than 0.01, the trend was considered to be significant. If not, no trend was reported for the particular station and constituent. If a significant trend was indicated, each individual coefficient was included in the reported trend, whether or not the individual significance level for the coefficient was less than 0.01.

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Appendix 2. Fitted Trends and Generalized Likelihood Ratio Test Results

For the trend results given in tables 2–1 through 2–6, the time interval of the trend is expressed in discrete calendar years although the time index in the previous section was expressed in decimal years. For example, a trend with m=1980 and w=2.5 extends from decimal year 1977.5 to decimal year 1982.5—that is, from mid-1977 to mid-1982. The time interval of the trend is specified as 1977-82 with the understanding that the trend extends from the middle of the first year (about July 1) to the middle of the last year. The estimated change in concentration for a particular trend interval is expressed as the percent difference between the median concentration at the end of the interval and the median concentration at the beginning of the interval. Using equation 1–8 (including the constant; eq. 1–5) and equation 1–9 and noting that the trend is for log-trans-

formed concentration, the median concentration for the end of the *j*th trend interval was expressed as

$$MC_j = 10^{(\alpha_0 + \gamma_1 + \gamma_2 + \dots + \gamma_j)}$$
 (1–14)

where

 MC_j is the median concentration for the end of the *j*th interval.

The percent change was computed as

$$100 \frac{(MC_j - MC_{j-1})}{MC_{j-1}} = 100(10^{\gamma_j} - 1). \tag{1-15}$$

Table 2–1. Fitted trends for standardized dissolved sulfate concentrations.

[+, positive change; <, less than; -, negative change; --, not applicable]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
1	05051522	Red River of the North at Hickson, North Dakota	1980-89	+109	<0.0001	<0.0001
2	05053000	Wild Rice River near Abercrombie, North Dakota	1977-82 1982-92	-51 +91	<.0001 .0005	<.0001
3	05059000	Sheyenne River near Kindred, North Dakota	1977-82 1987-92	-7.3 +21	.0873 .0001	.0009
4	05064500	Red River of the North at Halstad, Minnesota	1987-92	+11	.0065	.0065
5	05066500	Goose River at Hillsboro, North Dakota	No trend			
6	05079000	Red Lake River at Crookston, Minnesota	1972-77 1977-82	-32 +76	.0601 <.0001	<.0001
7	05085000	Forest River at Minto, North Dakota	1982-92	+48	<.0001	<.0001
8	05090000	Park River at Grafton, North Dakota	1982-92	+22	<.0001	<.0001
9	05102500	Red River of the North at Emerson, Manitoba	1977-82 1982-92	-30 +70	.0009 <.0001	<.0001

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 Table 2–2.
 Fitted trends for standardized dissolved chloride concentrations.

[+, positive change; <, less than; -, negative change; --, not applicable]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
1	05051522	Red River of the North at Hickson, North Dakota	1980-89	+105	<0.0001	<0.0001
2	05053000	Wild Rice River near Abercrombie, North Dakota	1977-82 1982-92	-41 +71	<.0001 .0011	.0004
3	05059000	Sheyenne River near Kindred, North Dakota	1977-82 1987-92	-29 +19	<.0001 .0037	<.0001
4	05064500	Red River of the North at Halstad, Minnesota	1987-92	+38	<.0001	<.0001
5	05066500	Goose River at Hillsboro, North Dakota	No trend			
6	05079000	Red Lake River at Crookston, Minnesota	1972-77 1977-82	-30 +57	.0203 <.0001	<.0001
7	05085000	Forest River at Minto, North Dakota	No trend			
8	05090000	Park River at Grafton, North Dakota	No trend			
9	05102500	Red River of the North at Emerson, Manitoba	1977-82 1982-92	-17 +40	.2018 .0048	.0016

 Table 2–3.
 Fitted trends for standardized dissolved-solids concentrations.

[+, positive change; -, negative change; <, less than; --, not applicable]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
1	05051522	Red River of the North at Hickson, North Dakota	1980-89	+23	0.0034	0.0034
2	05053000	Wild Rice River near Abercrombie, North Dakota	1977-82 1982-92	-35 +62	<.0001 .0009	<.0001
3	05059000	Sheyenne River near Kindred, North Dakota	1977-82 1987-92	-4.2 +9.4	.1977 .0058	.0041
4	05064500	Red River of the North at Halstad, Minnesota	1987-92	+10	.0019	.0019
5	05066500	Goose River at Hillsboro, North Dakota	No trend			
6	05079000	Red Lake River at Crookston, Minnesota	1972-77 1977-82	-8.3 +16	.1853 .0024	.0095
7	05085000	Forest River at Minto, North Dakota	1982-92	+21	.0017	.0017
8	05090000	Park River at Grafton, North Dakota	1982-92	+27	.0002	.0002
9	05102500	Red River of the North at Emerson, Manitoba	1977-82 1982-92	-10 +24	.1420 <.0001	<.0001

 Table 2–4.
 Fitted trends for standardized dissolved nitrite plus nitrate as nitrogen concentrations.

[-, negative change; +, positive change; --, not applicable; <, less than]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
3	05059000	Sheyenne River near Kindred, North Dakota	1982-92	-19	0.0100	0.0100
4	05064500	Red River of the North at Halstad, Minnesota	1982-92	+23	.0045	.0045
6	05079000	Red Lake River at Crookston, Minnesota	No trend			
9	05102500	Red River of the North at Emerson, Manitoba	1982-92	+27	<.0001	<.0001

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 Table 2–5.
 Fitted trends for standardized total ammonia plus organic nitrogen concentrations.

[-, negative change; <, less than; +, positive change; --, not applicable]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
1	05051522	Red River of the North at Hickson, North Dakota	1982-92	-62	<0.0001	<0.0001
3	05059000	Sheyenne River near Kindred, North Dakota	1977-82 1982-92	+72 -51	<.0001 <.0001	<.0001
4	05064500	Red River of the North at Halstad, Minnesota	1977-82 1982-92	+25 -26	.0536 .0024	<.0001
6	05079000	Red Lake River at Crookston, Minnesota	No trend			
9	05102500	Red River of the North at Emerson, Manitoba	1977-82 1982-92	+46 -37	.0038 <.0001	<.0001

Table 2–6. Fitted trends for standardized total phosphorus concentrations.

[--, not applicable; +, positive change; -, negative change]

Site number (figure 1)	U.S. Geological Survey station number	Station name	Time interval of trend	Estimated change in concentration (percent)	P-value for individual trend coefficient	P-value for combined trend coefficients
1	05051522	Red River of the North at Hickson, North Dakota	No trend			
3	05059000	Sheyenne River near Kindred, North	1977-82	+21	0.1188	0.0017
		Dakota	1982-92	-37	.0009	
4	05064500	Red River of the North at Halstad, Minnesota	No trend			
6	05079000	Red Lake River at Crookston, Minnesota	1982-92	-46	.0063	.0063
9	05102500	Red River of the North at Emerson, Manitoba	No trend			